NASA CR-72268

SEMI-ANNUAL REPORT

DEVELOPMENT OF HIGH-PERFORMANCE LIGHT-WEIGHT ELECTRODES FOR HYDROGEN-OXYGEN FUEL CELLS

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prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

July 15, 1967

CONTRACT NAS 3-8524

Period Covered: July 1, 1966 - December 31, 1966

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ABSTRACT

The overall objective of this contract effort is to determine and recommend preferred matrix materials and operating conditions under which American Cyanamid AB-40 electrodes would be capable of 2000-hour performance, in a total module having a weight-to-power ratio substantially lower than those presently available for space environment.

Several new matrix materials were evaluated and included in a life testing program. The electrodes and matrices were life-tested in small cells at current densities up to 600 ma/cm^2, and factors contributing to performance stability investigated.

A new, five-station, facility for life testing in battery-size single cells was designed, constructed and checked out. Cell assembly problems were studied.

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1. SUMMARY

Research effort was directed toward determining and recommending the combination of matrix materials and operating conditions most likely to result in high sustained performance of American Cyanamid AB-40 electrodes for 2000 hours or more at temperatures up to 200°C, pressures up to 60 psig and current densities up to 1000 ma/cm^2. The experimental program included preliminary evaluation of potentially suitable matrix materials and life testing at atmospheric pressure and at 45 psig. The major findings of this program are summarized below:

I. SMALL CELL TESTING

A. PRELIMINARY MATRIX EVALUATION

1. Matrices available at the start of the contract period included Fuel Cell Asbestos and Quinterra Asbestos which provide stable performance for more than 2000 hours at 100°C, and Ceria-PTFE which yields stability for approximately 1200 hours at 125°C and 400 hours at 150°C. Accordingly, several new matrices were introduced into the program with the approval of the NASA Project Manager for the primary purpose of obtaining stability for at least 2000 hours at temperatures above 100°C. These included Ceria-PTFE-PCTFE,[(a)] potassium titanate-PTFE, PTFE-PCTFE, and PTFE. All possess either a very good or a satisfactory combination of porosity (75-85%), ohmic resistivity (0.06-0.16 ohm-cm^2), and room temperature bubble pressure (7-30 + psig) and exhibit negligible shrinkage in water or in KOH at room temperature.

(a) Cerium oxide - polytetrafluoroethylene - polychlorotrifluoroethylene

2. Corrosion tests indicated the Ceria-PTFE-PCTFE and the potassium titanate-PTFE matrices to be potentially useful up to 150°C and 100-125°C respectively. Based on published corrosion data the PTFE-PCTFE and PTFE matrices are potentially useful up to 150°C and 200°C respectively.

B. ATMOSPHERIC PRESSURE LIFE TESTING

1. Atmospheric pressure life tests were conducted in 26 cm^2 active area cells. Major emphasis was placed on attaining (1) stable performance with the Fuel Cell Asbestos, Quinterra Asbestos and Ceria-PTFE matrices for current densities at which stable performance had not been achieved for any period of time under the previous NASA contracts[1,2] (i.e. at current densities above 100, 300 and 200 ma/cm^2 respectively) and (2) stable performance with the new matrices at temperatures above 100°C. For this program, stability was defined as a voltage loss not exceeding 80 mv during 2000 hours. Accordingly, the voltage decline rate should not exceed 4.0 mv/100 hours.

2. In a test which had started under the previous contract,[2] the Fuel Cell Asbestos matrix yielded stable performance at 100 ma/cm^2 for 9700 hours at 0.94-0.78 v. Stability with this matrix was extended to 200 ma/cm^2 for 600 hours and to 300 ma/cm^2 for 400 hours. The voltage level at 300 ma/cm^2 was 0.84 v.

3. Stable performance was achieved in duplicate tests with the Quinterra Asbestos matrix at very high current density (400 ma/cm^2) for 1000-1300 hours. Near-stable performance was attained for 2000 hours. The voltage, initially 0.85 v, was 0.73-0.76 v at the end of the 2000 hour period.

Considerable progress was made toward achieving stability at still higher current density (600 ma/cm^2) with this matrix. The lowest overall decline rate was 8 mv/100 hours during nearly 700 hours at a voltage level of 0.77-0.72 v.

4. At least part of these improvements in stability are obtained by minimizing electrolyte concentration gradients from anode to cathode. Gradients below four percent KOH can be maintained even at 600 ma/cm^2 (Quinterra Asbestos matrix) by: (1) humidifying the inlet reactant gases at dew points yielding equilibrium concentrations not more than 5% KOH above the nominal concentration, (2) employing nominal concentrations close to that yielding maximum conductivity and (3) minimizing the diffusion path without causing matrix breakage or gas cross leaks.

5. The Ceria-PTFE matrix has not yielded stable performance in tests at 125°C and 300 ma/cm^2. Voltage decline rates were mostly 6-7 mv/100 hours during 400-700 hours at average voltages of 0.83-0.88 v.

6. The Ceria-PTFE-PCTFE matrix was found to be unsuitable for long term performance at 125°C because it repeatedly broke within 400 hours after test start-up.

C. PRESSURE LIFE TESTING

1. Especially high stable performance was achieved in 26 cm^2 active area cells at 45 psig for periods up to 1300 hours, limited mostly by mechanical difficulties. Stable voltages at 100°C (Quinterra Asbestos matrix) and 125°C (Ceria-PTFE matrix) were 0.98-0.99 v

at 100 ma/cm^2 and 0.94-0.95 v at 200 ma/cm^2 with 50% KOH electrolyte. Operation at higher electrolyte concentration (60%), at 125°C, raised the stable voltages to 1.02 v and 0.99 v respectively.

II. LARGE CELL TESTING

1. A new five station facility for life testing battery-size electrodes was designed and constructed. The stations can be operated with either dry or humidified gases at pressures up to at least 60 psig.

2. Several test cells, unsuitable at the start of the contract, were modified to permit greater compression of the matrix and to protect against hydraulic rupture of the matrix in the segment area.

3. Gas cross-leakage prevented test start-up in a large number of assemblies with 20 mil Quinterra Asbestos matrices. Examination of the disassembled cells showed physical breakage of the matrix in many instances. Better sealing was obtained with 30 mil thicknesses of the matrix.

4. Two life tests with Fuel Cell Asbestos and Ceria-PTFE matrices using dry inlet gases had high voltage decline rates.

2. INTRODUCTION

2.1 Prior Work

Light-weight fuel cell batteries capable of producing large quantities of energy appear feasible for space applications. High performance light-weight electrode systems are an essential part of these batteries. Work completed previously[1,2] under NASA Contracts NAS 3-2786 and NAS 3-6477 showed that American Cyanamid AB-40 electrodes give high and sustained performance in alkaline matrix-type fuel cells operating on hydrogen and oxygen. It was established that substantial initial performance advantages are obtained at current densities up to 300-400 ma/cm^2 by employing high electrolyte (KOH) concentrations (50-80%). Intermediate temperatures (100-200°C) are required or are preferable for operation at these concentrations and are also potentially advantageous for the removal of waste heat and product water from a battery system. At all current densities, operation at intermediate pressures (45-60 psig) provides substantial gains in initial performance without significantly increasing the estimated weight of a battery system. Highest initial working voltages obtained at current densities of 100, 400 and 1000 ma/cm^2 were 1.10 v, 0.95 v and 0.82 v respectively when the electrodes are separated by a matrix of average resistance (ACCO-II Asbestos).

It was shown that attainment of these performance levels for sustained long term operation depends primarily on the availability of a suitable matrix. Asbestos matrices (Fuel Cell Asbestos, Quinterra Asbestos,

ACCO-I and ACCO-II Asbestos) available at the start of Contract NAS 3-6477 imposed an upper temperature limit of approximately 100°C for long term operation. A new proprietary matrix (Ceria-PTFE) extended this limit to at least 125°C but not to 150°C. With these matrices, high performance was sustained in 26 cm^2 active area cells at atmospheric pressure for 1200 hours or more, both at 100°C for current densities up to 300 ma/cm^2, and at 125°C for current densities up to 200 ma/cm^2. Performance stability was demonstrated at higher temperature (150°C) for up to 400 hours, and at higher pressure (45 psig) for up to 580 hours. A battery-size cell (234 cm^2 active area) was operated stably at atmospheric pressure for 1000 hours. Based on the sustained performance level achieved either at atmospheric pressure (0.97-0.87 v at 100-300 ma/cm^2 respectively) or at 45 psig (1.03-1.00 v at 100-200 ma/cm^2 respectively), it was estimated that a total 2 KW module which might incorporate the AB-40 electrodes would weigh, exclusive of fuel and related tankage, less than 50 LB/net KW.

Attainment of still better sustained performance appeared to depend on the further development of improved matrices capable of operating at 150-200°C and/or at current densities above 300 ma/cm^2.

2.2 Objectives

The primary objective of this contract is to determine and recommend the combinations of matrix materials and operating conditions most likely to result in the high sustained performance of AB-40 electrodes for 2000 hours or longer at temperatures up to 200°C, pressures

up to 60 psig and current densities up to 1000 ma/cm^2. Performance stability is defined as a voltage loss not exceeding 80 mv during 2000 hours.

2.3 Scope

The scope of work to be done by American Cyanamid Company is shown in the following description which is a condensation of the Schedule of Work for Contract NAS 3-8524.

The contractor shall make available, a total of five (5) 6" x 6" active area pressure cells, and four (4) 2" x 2" active area pressure cells and their associated test rigs. The nine designated cells will be used to perform continuous life tests under conditions approved by the NASA Project Manager. Cells which operate satisfactorily will continue on test for 2,000 hours, after which new cells will be substituted so that the maximum amount of testing can be accomplished within the period of performance. Atmospheric pressure endurance tests shall be performed in the twelve (12) 2" x 2" cells which were made available during Contracts NAS 3-2786 and NAS 3-6477.

As a parallel effort performed over the first six months of the contract period, the contractor shall investigate promising electrolyte matrix materials. Materials will be evaluated first by immersion in KOH solutions. Those which perform satisfactorily will be tested in 2" x 2" atmospheric pressure fuel cells and if still promising, will be factored into the life test program.

At the conclusion of the life test program, the contractor shall recommend operating conditions which appear to deliver the best combinations of cell life and efficiency.

3. SMALL CELL TESTING

Small cell testing included preliminary matrix evaluations and life testing at atmospheric pressure and at 45 psig. "Two-inch cells" having an active area of 26 cm^2 were used in this work.

3.1 AB-40 Electrodes

American Cyanamid AB-40 electrodes, used as both anode and cathode, were employed previously under NASA Contracts NAS 3-2786 and NAS 3-6477: In the former contract they were known as "high loading electrodes". The electrodes contain 40 mg Pt catalyst/cm^2 and one third as much PTFE used as a binder-waterproofing agent. This waterproofing and a high degree of porosity in the electrodes provide suitable contact among gas, catalyst and electrolyte. The catalyst-waterproofing mixture is supported on a 24 mesh, 14-mil wire, nickel screen plated with 0.05 mil of high temperature gold. The electrodes are 28 mils thick.

3.2 Preliminary Matrix Evaluations

The evaluation of matrix materials was aimed at extending the temperature range for stable performance up to 125-200°C for 2000 hours or more. Towards this end, four new proprietary matrices, similar in structure to the Ceria-PTFE matrix, were introduced into the evaluation program. They included (1) 90/5/5 Ceria-PTFE-PCTFE, (2) 95/5 Potassium Titanate-PTFE, (3) 50/50 PTFE-PCTFE and (4) PTFE. Both of the all-fluorocarbon matrices do not wet in KOH. Therefore, they were wetted by

incorporating either of two commercial perfluorinated surfactants, designated FC-95 and FC-128 (3 M Company), in the electrolyte. These surfactants appear to be potentially most suitable for use at temperatures up to 150-200°C. Table 3-1 compares the properties of the new matrices with those of the Ceria-PTFE matrix. All possess a good combination of high porosity, low ohmic resistance, and high bubble pressure at room temperature. The Ceria-PTFE-PCTFE and potassium titanate-PTFE matrices have approximately the same bubble pressure and cell resistance as the Ceria-PTFE matrix. The PTFE-PCTFE matrix has similar bubble pressure and somewhat lower resistance. The PTFE matrix has lower bubble pressure and higher resistance.

Like the Ceria-PTFE matrix, the new matrices as prepared are saturated with water and are equilibrated directly in KOH solution at room temperature before being assembled in the cell. The Ceria-PTFE matrix shrinks in water, losing 17-23% of its area. Equilibration of the matrix in 50% KOH causes an additional area loss of 10%. The four new matrices have better room temperature shrinkage properties, losing less than 10% of their area in water or in KOH. All five matrices stop shrinking within 70 hours. Greater shrinkage occurs at higher operating temperature (125°C) and KOH concentration (60%). Figure 3-1 shows the loss of area with time for each matrix. The data for each curve is averaged from 3-6 samples of a given matrix batch. Two different batches were tested for all matrices except Ceria-PTFE. Within periods up to 330 hours, the PTFE matrix loses less of its area (15-30%) than the Ceria-PTFE, Ceria-PTFE-PCTFE, and

PTFE-PCTFE matrices (40-62%). Nearly all of this shrinkage occurs within the first 70 hours. The potassium titanate-PTFE matrix has approximately the same loss of area as the PTFE matrix during 190 hours. Thereafter this loss accelerated to 50%.

Beaker corrosion tests were run with the Ceria-PTFE-PCTFE and potassium titanate-PTFE matrices at 100-200°C and 50-75% KOH, mostly for 500 hours. Results are shown in Table 3-1. The Ceria-PTFE-PCTFE matrix lost 1.4% of its weight at 100°C and 6.5% at 150°C and disintegrated physically into a precipitate at 200°C. These data indicated the matrix to be potentially suitable over at least some portion of the range 100-150°C. The potassium titanate-PTFE matrix lost 10.5% of its weight at 100°C, 18% at 150°C, and approximately 61%, within 140 hours, at 200°C. Although the corrosion resistance of the potassium titanate-PTFE matrix is not outstanding even at 100°C, it was considered sufficient to warrant life-testing of this matrix at 100-125°C.

3.3 LIFE TESTING

Small cell life tests are conducted to obtain sustained high performance at the highest current densities and temperatures feasible with available matrices. Stability is defined in Section 2.2 as a voltage loss not exceeding 80 mv during 2000 hours. Accordingly, the overall voltage decline rate should not exceed 4.0 mv/100 hours. A secondary objective is the determination of operating variable effects on performance stability.

Life tests at atmospheric pressure and at pressures above atmospheric are discussed separately below.

3.3.1 Atmospheric Pressure Life Testing

3.3.1.1 Test Conditions

During the current period, major emphasis was placed on (1) attaining stable performance with previously available matrices (Fuel Cell Asbestos, Quinterra Asbestos, and Ceria-PTFE) at current densities above those achieved under the prior NASA contract[2] (i.e., above 100, 300 and 200 ma/cm^2 respectively) and (2) attaining stable performance with new matrices at temperatures above 100-125°C.

Tests were conducted at 90-150°C, 30-67% KOH and 100-600 ma/cm^2 with humidified inlet gases. In all tests, the electrodes were pre-wet with electrolyte, to 15-25% of their weight, before they were assembled in the cell.

3.3.1.2 Test Cells and Stations

The tests are carried out in gasketted flat-plate cells at 10 stations equipped with water saturators for humidifying both hydrogen and oxygen. The cell and station designs have been described previously[1,2] in detail. The hydrogen is a pre-purified grade (Airco) containing approximately 3 ppm CO_2, 1 ppm CO and 0.1 ppm O_2. The oxygen (Airco) contains approximately 5 ppm of CO_2. In order to remove CO_2, both gases

are passed through Ascarite scrubbers in the gas manifold and then through liquid caustic scrubbers located at each station. The Ascarite is changed if it whitens, indicating a loss of activity. Caustic solutions are changed every 2-5 days depending on the gas flow rate, if they become cloudy from carbonate precipitation or too concentrated and cause foaming.

3.3.1.3 Test Procedures

Prior to start-up, a polarization curve is run on dry gases at current densities up to 1000 ma/cm^2. The test is then run on humidified gases at constant current. Cell voltage and temperatures are monitored continuously and are recorded daily. Cell internal resistance and saturator temperatures are recorded daily.

Product water formed by the cell reaction is removed by vaporization into an excess flow of reactant gases. In nearly all tests, both gases enter the cell at the same dew point. Under these conditions, the total flow of inlet gas is computed from Equation (1).

$$Fi = \frac{7.6\ I\ (1 + 1.5\ Ye)}{Ye = Yi} \qquad (1)$$

where Fi = total inlet flow of $H_2 + O_2$ (cc/min at 23°C + 0 psig)

I = cell current (amps)

$$Yi = \text{humidity of inlet gas} \left[\frac{\text{moles } H_2O}{\text{mole gas}}\right] = \frac{Pi°}{760 - Pi°}$$

$$Ye = \text{humidity of exit gas} \left[\frac{\text{moles } H_2O}{\text{mole gas}}\right] = \frac{Pe^\circ}{760 - Pe^\circ}$$

where Pi° and Pe° = vapor pressure of water (mm) in the inlet gases and in the cell respectively.

The vapor pressure of the inlet gases depends on the saturation temperature. The cell vapor pressure depends on the cell temperature and the nominal KOH concentration to be maintained. Vapor pressures at 100°C and 30-60% KOH were taken from the International Critical Tables.[3] Vapor pressures at 125-200°C and 50-80% KOH were taken from established extrapolations.[4]

The flow of each reactant gas leaving the cell is calculated according to Equations (2) and (3)

$$\text{for hydrogen: } F_{eH} = \left[\frac{S}{S+1}\right] F_i - 7.6\ I \qquad (2)$$

$$\text{for oxygen: } F_{eO} = \frac{F_i}{S+1} - 3.8\ I$$

where $F_{eH} + F_{eO}$ = exit flow rates of

$$H_2 \text{ and } O_2 \text{ respectively} \left[\frac{cc}{min} \text{ at } 23^\circ C \text{ \& } 0 \text{ psig}\right]$$

$$S = \text{inlet flow ratio of } H_2/O_2 \left[\frac{cc}{cc}\right] \qquad (3)$$

The exit flows are measured at least twice weekly with high accuracy by means of a Vol-U-Meter flow rate calibrator (G. H. Porter, Inc.) and adjusted if necessary to the proper level. In addition, approximate checks of all gas flow rates are made at least daily using precision rotameters.

3.3.1.4 Test Results

Table 3-2 summarizes test conditions and results. The table shows initial and final voltages and average voltage decline rates. The "initial voltage" is the maximum voltage obtained within 100 hours after the start of the test. In most runs where the electrolyte was not concentrated within the cell (30-50% KOH), the initial voltage was the same as the voltage when the cell was first put on load. In runs where the electrolyte was concentrated within the cell (55-67% KOH), the initial voltage generally rose to a maximum level. The "average voltage decline rate" was taken from the average slope of a voltage-time plot. In most runs, the overall decline rate was well defined despite small fluctuations. Where these fluctuations were large, the decline rate is listed as "erratic." The decline rate is listed as "accelerated" in those few tests where it accelerated throughout part or all of the test period. Where the voltage decline rate changed during a test, each decline rate is noted separately. The "final voltage" is the voltage at the end of a period of defined average voltage decline rate. In most

runs, this was also the voltage at the time the test was terminated. An additional "final voltage" is shown at the end of 2000 hours for most of the tests which ran for that length of time.

Figures 3-2 through 3-15 show voltage-time and resistance-time curves for nearly all tests which ran more than 100 hours. Test results are discussed below according to matrix type.

3.3.1.4.1 Test with ACCO-I Asbestos Matrix

Test 2-357, started during the previous contract at 100°C and 100 ma/cm^2 ran stably for 5000 hours at 0.93-0.94 v (Figure 3-2). Throughout the test, not including the brief rise in voltage which occurred at 2800 hours from an inadvertent interruption in the oxygen feed, the voltage decline rate was 0.4 mv/100 hours. After 5000 hours, the test was terminated to make the station available for new tests.

3.3.1.4.2 Tests with Fuel Cell Asbestos Matrix

Test 2-324 was started under the previous contract with Fuel Cell Asbestos at 100°C and 100 ma/cm^2. Performance was very stable for 9700 hours at an overall decline rate of 1.6 mv/100 hours (Figure 3-3). Thereafter, the decline rate accelerated and the test was terminated.

Previous, unstable, tests at 200-300 ma/cm^2 with Fuel Cell Asbestos[2] were conducted with a 20 mil thickness of the matrix at 100°C and 50% KOH. The reactant gases had entered the cell in counter-current flow, humidified at dew points (45-55°C) which limited the maximum

equilibrium KOH concentration to only 5-10 weight percent below the solubility limit (65%). Under these conditions, voltage decline rates were 7-25 mv/100 hours at 200 ma/cm^2 and mostly 20-30 mv/100 hours at 300 ma/cm^2. Instability was at least partly caused by the relatively high KOH concentration gradients (mostly 4-12%) which formed from anode to cathode. Under the present contract, lower decline rates were obtained at 200-300 ma/cm^2 when the concentration gradient was reduced to below 4% (Table 3-3). This was accomplished by one or more of the following changes that were made in the operating conditions (1) reduction of the nominal electrolyte concentration to 30-40% (either with or without a simultaneous reduction in temperature to 90-93°C) in order to increase its conductivity (2) increasing the difference between the maximum equilibrium KOH concentration and the solubility limit to 20-28% by humidifying the inlet gases at higher dew points (70-72°C) (3) reduction of the electrolyte diffusion path through use of a thinner (15 mil) matrix and (4) operation with co-current gas flow, mostly with the oxygen feed nearly dead-ended (exit H_2/O_2 ratio = 12-18).

Figure 3-4 shows tests at 200 ma/cm^2. Initial voltages were mostly in the range 0.86-0.88 v. Tests 2-479, 2-476, 2-463 and 2-458 operated with the usual 20 mil thick matrix at 35-40% KOH, over a range of exit H_2/O_2 ratios (1-12) and KOH loadings in the matrix (1.5-2.5 g/g matrix). (Test 2-458 was run first at 300 ma/cm^2 for 400 hours). At the usual KOH loading (1.5 g/g) voltage decline rates were 4.0-7.7 mv/100

hours for periods of 328-620 hours. The decline rate in one of these tests (2-479) then accelerated. At the higher KOH loading, the decline rate accelerated throughout the test (2-476). Test 2-477, employing a 15 mil matrix at 40% KOH and the high KOH loading, had a decline rate of 5.9 mv/100 hours during 640 hours. Thereafter the decline rate accelerated.

Tests at 300 ma/cm^2 are shown in Figures 3-5 and 3-6. Initial voltages were mostly in the range 0.83-0.86 v. Six tests had decline rates below 10 mv/100 hours for periods of 400-900 hours. One of these tests (2-487), operating with a 15 mil matrix at 30% KOH was very stable for 400 hours at 0.84 v and a decline rate of 1.5 mv/100 hours. The test then became unstable following an inadvertent admission of air to the anode through the hydrogen saturator.

It can be seen that better stability at 300 ma/cm^2 was obtained at 90°C and 30% KOH than at 100°C and 40% KOH either with 15 mil matrices (TLT-2-484, - 478 and -474) or with 20 mil matrices (TLT-2-491, -458 and 463) under otherwise identical conditions. Additional work is required to separate the temperature and concentration effects. Nevertheless, the improvement in performance caused by decreasing the concentration alone, from 50% to 40% KOH, at 100°C, indicates that the further reduction to 30% KOH was at least partly responsible for improved stability.

Reducing the matrix thickness from 20 mils to 15 mils improved stability at 100°C and 40% KOH (TLT-2-478, -474, -458 and -463) and (TLT-2-473 and -475). No significant effect of thickness was noted in two tests at 90°C and 30% KOH (TLT-2-484 and -491).

At both thicknesses, a KOH loading of 2.5 g/g matrix gave very low initial performance and much poorer stability than the usual loading of 1.5 g/g. Reducing the loading to 1.0 g/g improved stability, with the 15 mil matrix (TLT-2-487 and -484).

3.3.1.4.3 Tests with Quinterra Asbestos Matrix

Figure 3-7 shows tests with 20 mil Type 10 Quinterra Asbestos at 200-300 ma/cm^2.

At 200 ma/cm^2, test 2-420 passed contract specifications, running stably for 2000 hours at 0.89-0.82 v at a decline rate of 3.4 mv/100 hours. The test was terminated at 2320 hours after caustic solution from a scrubber accidentally entered the cell. Test 2-425 was stable for 1100 hours at 0.89-0.84 v. The decline rate then became unstable (6.3 mv/100 hours) during 1100-2800 hours. (Within this interval a 70 mv voltage rise, at 1400 hours, was caused by an inadvertent interruption in the oxygen feed.) The decline rate then accelerated and the test was terminated.

At 300 ma/cm^2, one test was very stable for 1000 hours at 0.84-0.83 v with a decline rate of 1.4 mv/100 hours (2-421). The decline rate was high (6.5 mv/100 hours) during 1000-2150 hours and then became erratic.

At current densities above 300 ma/cm^2, voltage stability was improved by lowering the KOH concentration to 30-40% and raising the inlet gas dew points to 72°C. (This effect is similar to that described

above for the more dense Fuel Cell Asbestos at current densities above 100 ma/cm^2 and is probably due mostly to the resulting higher conductivity of the electrolyte.)

Tests at 400 ma/cm^2 are shown in Figure 3-8. All but one employed a lower KOH loading (2.0 g/g matrix) than did the tests at lower current densities (3.0 g/g matrix) since this lower loading gives much higher initial performance at 400 ma/cm^2. Thus in four tests at the reduced loading, the initial voltage was 0.82-0.85 v compared to 0.77 v at the higher loading. The latter voltage level agrees with those obtained under the same conditions in previous work.[2]

Near-stable performance was obtained for 2000 hours in duplicate tests operating at 100°C and 40% KOH. Thus test 2-446 was stable for 1360 hours at 0.84-0.80 v. Thereafter, this rate increased to 7.2 mv/100 hours so that after 2000 hours, the overall decline rate was 4.5 mv/100 hours. Test 2-451 was nearly stable for 1300 hours at 0.85-0.79 v and a decline rate of 4.5 mv/100 hours. This rate then increased to 8.0 mv/100 hours, thereby raising the overall decline rate after 2000 hours to 5.5 mv/100 hours.

By contrast, three tests at 50% KOH and inlet gas dew points of 55-61°C were unstable throughout their entire duration (TLT-2-445, -444 and -433). One of these (2-445), which was run under otherwise identical conditions as the tests at 40% KOH, had a decline rate of 7.4 mv/100 hours during 1000 hours. The decline rate then accelerated and the test was terminated.

Because of the encouraging results obtained at 400 ma/cm^2, life tests were run at 600 ma/cm^2. Eight tests employed different levels of KOH concentration (30-40 %), temperature (80-100°C), inlet gas dew point (59-81°C) and exit H_2/O_2 ratios (1-38). All employed an initial KOH loading of 2.0 g/g matrix. Initial voltages were mostly 0.76-0.80 v and averaged 0.78 v.

Figures 3-9, 3-10 and 3-11 show test results. Under constant load, the most promising decline rates (8-12 mv/100 hours for 690-430 hours) were obtained in three tests (2-470, -480 and -490) operating at 30% KOH and 80-90°C. By contrast, three tests (3-465, -455 and -457) which started at 35-40% KOH and 100°C either with the same H_2/O_2 flow ratio (38) or with a lower ratio (1.0) had higher decline rates (16-19 mv/100 hours).

In duplicate tests at 100°C and 40% KOH (2-468 and -469), water was fed to the cathode, by humidifying the oxygen stream at 81°C. This water and the product water were removed by the hydrogen stream humidified at 67°C. Both tests had accelerated decline rates.

It was found that although high voltage declines at 600 ma/cm^2 irreversibly decreased the voltage level at lower current densities, they had relatively little effect on performance stability at these lower current densities. Thus tests 2-455 and 2-457 had decline rates of 18-19 mv/100 hours for 300-500 hours. When the load was reduced to 400 ma/cm^2, the initial voltages were 40-70 mv lower than normal. Nevertheless, both

decline rates at 400 ma/cm^2 were stable or nearly stable (4.0-4.4 mv/100 hours) for 100-300 hours. (The decline rate in Test 2-455 became unstable after 100 hours when a saturator became plugged and was then un-plugged.) When test 2-455 was returned to 600 ma/cm^2 but at a higher flow ratio than at the start (6.0 instead of 1.0), the decline rate was nearly stable (5.0 mv/100 hours) for 240 hours and then accelerated. The load was then reduced to 100 ma/cm^2. Although the initial voltage (0.90 v) was 30-40 mv lower than normal, the voltage was very stable for 200 hours.

3.3.1.4.4 Tests with Ceria-PTFE Matrix

Nearly all tests with the 95/5 Ceria-PTFE matrix were run at 125°C. One test was run at 100°C in order to compare the performance of this matrix with that of the asbestos matrices. A test at 150°C was continued from the previous contract.

Figure 3-12 shows results at 200 ma/cm^2. Test 2-494 at 100°C and 50% KOH started at 0.91 v, declined to 0.88 v during the first 30 hours, and has been running stably for the past 200 hours. During this period, the performance level was the same as that of Quinterra Asbestos (tests 2-420 and 2-425). Two tests (2-428 and -430) operating at 125°C and 60% KOH were continued from the previous contract. Test 2-428 was stable for 930 hours at 0.93-0.90 v and then became unstable. Test 2-430 was unstable for the first 230 hours and then became very stable for the next 240 hours at 0.91 v. Following an inadvertent drop in temperature to 110°C for three hours, the voltage rose to 0.94 v and then declined at an unstable rate (6.5 mv/100 hours).

Tests at 125°C and 300 ma/cm^2 are shown in Figure 3-13. In three tests at 60% KOH, the average initial voltage (0.88 v) was 20 mv higher than in three tests at 55% KOH. Five of these tests (2-454, -460, -434, -435 and -438) declined at nearly the same rate (6-7 mv/100 hours) for periods of 400-700 hours. The sixth test (2-449) declined at an accelerated rate.

One additional test (2-447) at 60% KOH employing a higher inlet gas dew point (61°C instead of 55°C) and a higher H_2/O_2 exit ratio (6.0 instead of 1.0) than the other three, declined at a very high rate for 140 hours. When the gas flow rates were changed to give a 1.0 H_2/O_2 ratio, and a slightly reduced nominal KOH concentration, the decline rate was nearly stable (5.0 mv/100 hours) for 280 hours.

In all tests but one, the cell resistance remained nearly constant which indicates that little of the electrolyte had reacted with the matrix. Nevertheless, in four tests the matrix broke along one or more edges of the electrodes, following the period of defined voltage decline. Breakage caused gas cross-leaks which resulted in either an accelerated decline or sudden test failure.

One test (2-441) was run at 150°C and 100 ma/cm^2 at 67% KOH (Figure 3-14). For 400 hours, the voltage was nearly stable at 1.00-0.98 v and a decline rate of 5.5 mv/100 hours. The matrix then broke and the test was terminated. These results confirm the conclusion reported previously[2] that the present configuration of this matrix is unsuitable for long term operation at 150°C.

3.3.1.4.5 Tests with Ceria-PTFE-PCTFE Matrix

Figure 3-15 shows tests with the 90/5/5 Ceria-PTFE-PCTFE matrix at 125°C, 50% KOH and 200 ma/cm^2. Good initial performance resulted when the saturation KOH loading in the matrix (1.1-1.3 g/g matrix) was reduced to 0.6-1.0 g/g by loading 30-40% KOH into the electrodes and matrix and then concentrating to 50% during the initial polarization curve. In all tests performance was unstable and the matrix broke within 400 hours after start-up. In one test at 150°C, 67% KOH and 100 ma/cm^2, the performance was unstable and the matrix broke within 120 hours.

These results demonstrate that the present configuration of this matrix is unsuitable for long term operation at 125-150°C.

3.3.1.4.6 Test with Potassium Titanate-PTFE Matrix

Test 2-495 was started with the 95/5 Potassium Titanate-PTFE matrix at 125°C, 50% KOH and 200 ma/cm^2. The initial voltage was 0.88 v. The test has run 66 hours and is continuing.

3.3.1.5 KOH Concentration Gradient

The cell reaction creates KOH concentration gradients within the electrodes and the matrix. An "overall" concentration gradient across the electrode-matrix sandwich was measured at least once in nearly all tests. In most tests, operating with co-current gas flow, this gradient was across the exit end of the sandwich. In the few tests

with counter-current flow, the measured gradient extended diagonally through the sandwich. The magnitudes of these gradients were estimated from the humidity of the hydrogen and oxygen streams leaving the cell, assuming water vapor equilibrium between electrolyte and exit gas. Humidities were measured by weighing the water collected from the gases, at known flow rates, in Drierite tubes. Equilibrium KOH concentrations and overall gradients are shown in Table 3-3. In most tests where the gradient was determined more than once, it remained nearly constant with time (within two weight percent) for intervals as long as 1900 hours.

As is to be expected for an alkaline fuel cell, the concentration at the cathode was nearly always greater than at the anode. The major exception occurred in Test 2-324 during the period 5700-9400 hours. Whereas for the first 4000 hours of this test, the direction of the gradient had been normal,[2] all exit gas humidity measurements made during the interval showed a reversal in direction followed by a return to the normal gradient direction. The reason for these reversals is not yet apparent.

It can be seen that in the great majority of tests, 32 out of 42, the gradient was small (less than 4%) even at current densities as high as 400-600 ma/cm^2. This resulted primarily from the use of humidified inlet gases. Thus in tests with the Quinterra Asbestos matrix at 200-300 ma/cm^2 with dry gases (Tests -2-420, -425 and -421), the average gradient was 8.2-9.7%. Operation with humidified gases at 400 ma/cm^2, at

which current density the gradients would be expected to be even higher, reduced the average gradient to 3.0-4.5% (Tests 2-445, -433 and -444).

The low level of this overall concentration gradient did not in itself guarantee voltage stability. Nevertheless, results obtained previously[2] indicate that they probably made possible the achievement of near-stable performance at 400 ma/cm^2 and promising stability at 600 ma/cm^2.

3.3.1.6 Carbonate Build-up During Life Tests

As described in Section 3.3.1.2, the hydrogen and oxygen used in these life tests were scrubbed first through Ascarite and then through caustic solution. The carbon dioxide remaining in the scrubbed gases converts some of the KOH within the cell to insoluble potassium carbonate. Since the gases are not recirculated and in most tests are fed to the cell at high flow rates (5-20 times stoichiometric) even trace quantities of carbon dioxide passing the scrubbers, could lead to a considerable build-up of potassium carbonate in long tests, particularly at high current densities. The extent of this build-up was determined at the end of a number of tests over a wide range of total gas flows. Figure 3-16 shows separate sets of data for tests with Fuel Cell Asbestos and Quinterra Asbestos matrices. With both matrices, the relationship between conversion and total gas flow is approximately linear. From the slope of the curve for the tests with Quinterra Asbestos, it is estimated that approximately 0.5 ppm carbon dioxide was absorbed from the inlet gases. Less extensive data for tests with the Fuel Cell Asbestos matrix indicate an absorption close to 1.5 ppm.

The extent to which the electrolyte can be converted to carbonate without causing unstable performance is of interest. Minimum conversions are estimated in Table 3-4 which combines the conversion data of Figure 3-16 with the life test data of Table 3-2 for tests which were stable with the highest total flow of reactant gases at a given current density. It can be seen that stability is possible for conversions up to at least 28% at 100 ma/cm^2 and up to at least 15% at 200-400 ma/cm^2. Subsequent instability in the tests at 100 and 400 ma/cm^2 was not necessarily due to additional carbonate build-up.

3.3.1.7 Crystallite Size of Life-Tested Electrodes

The fresh electrodes have an average platinum crystallite size of 95Å. The effect of prolonged operation on crystallite size was determined from X-ray diffraction measurements taken on the electrodes at the end of tests covering a wide range of cell temperature (80-150°C), current density (100-600 ma/cm^2) and operating time (140-10,200 hours). Table 3-5 shows crystallite sizes for the matrix side of these electrodes.

The cathode crystallite size was significantly higher (by 20-70Å) than that of the anode at 100°C and 400-600 ma/cm^2, at 125°C and 300 ma/cm^2 and at 150°C and 200 ma/cm^2. (The data at 150°C was reported previously.[2] At all lower current densities at these temperatures both electrodes had substantially the same crystallite size. It appears then that the current density at which the cathode crystallite size becomes significantly higher than that of the anode decreases with increasing temperature.

Using the data of Table 3-5, Figures 3-17 and 3-18 show the effects of time and temperature on the crystallite size of anode and cathode respectively. Within the first 800 hours, the crystallite size of the anode increases more rapidly at the higher temperatures while the rate of increase of crystallite size at the cathod is approximately the same at all temperatures. For test durations of 800-3200 hours, data were obtained at 90°C and 300 ma/cm^2, 100°C and 200-600 ma/cm^2 and at 125°C and 200 ma/cm^2. While these data are widely scattered, they indicate a general gradual rise in crystallite size to 155-165Å at both electrodes. The lone exception appears to be a decrease in crystallite size of the anode at 100°C and 400 ma/cm^2 to the level of fresh electrodes in three different life tests. The reason for this is not yet apparent.

The scatter of the data does not permit further correlation of crystallite size with current density.

TABLE 3-1

PROPERTIES OF NEW MATRICES

Matrix	Porosity (%)	Cell Resistance (milliohms)	Bubble Pressure (psig)	Loss of Area (%) In: Water At 23°C	50% KOH At 23°C	60% KOH At 125°C	Weight Loss[i] (%) During 500 Hours[j] In: 50% KOH At 100°C	65-70% KOH At 150°C	75% KOH At 200°C
90/5/5 CERIA-PTFE-PCTFE	80-85	12-15	13-19	3- 7	0- 7	40-52[a]	1.2- 1.6	6.5-6.6	(d)
95/5 POTASSIUM TITANATE-PTFE	83-85	16-20	17-30+	0- 3	0- 3	12-28[b] 50-57[c]	10.2-10.6	18.0	~ 61[e][f]
50/50 PTFE-PCTFE	75-83	10	14	0- 8	3- 7	58-62[c]	—	—	—
PTFE	75-76	32	7-10	3- 5	4	15-30[c]	—	—	—
95/5 CERIA-PTFE	75-80[h]	12-18[h]	16-20[h]	17-23	10	38-44[c]	—	4[h]	28[e][g][h]

(a) Within 70 hours
(b) Within 190 hours
(c) Within 300 hours
(d) Matrix disintegrated physically
(e) Some solids separated physically from matrix
(f) Weight loss after 140 hours
(g) Weight loss after 400 hours
(h) Data reported previously[2]
(i) Corrosion Samples (2-3 in. square) were immersed in 400 cc of KOH solution.
(j) 500 hours unless indicated otherwise.

TABLE 3-2

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE

Cell: Two Inch
Electrodes: AB-40

TLT No.	Current Density (ma/cm²)	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	Initial KOH Loading: g/g Matrix	Initial KOH Loading: Total[a] In Cell (g)	H_2-O_2 Flow Direction	Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate (cc/min At 23°C & 0 Psig): H_2	Inlet Gas Flow Rate (cc/min At 23°C & 0 Psig): O_2	Exit H_2/O_2 Ratio	Test[b] Duration (Hours)	Working Voltage(v): Initial[c]	Working Voltage(v): Final[b]	Average[b] Voltage Decline Rate (mv/100 hours)	Status	Reason For Termination
TEST WITH ACCO-I ASBESTOS MATRIX																	
2-357	100	100	50	20	3.1	4.8	Counter	45	74	74	0.8	5007	.943	.935	0.4	Terminated	(1)
TESTS WITH FUEL CELL ASBESTOS MATRIX																	
2-324	100	100	50	20	1.3	6.1	Counter	45	74	74	0.8	9700	.937	.784	1.6	Terminated	(2)
2-479	200	93	35	20	1.5	5.7	CO-	70	350	50	10	0- 500	.879	.842	5.4	—	
												560-1000	.842	.800	9.5	—	
												1000-1367	.800	.688	(j)	Terminated	(2)
2-477	200	100	40	15	2.5	6.3	CO-	72	390	50	12	0- 640	.883	.845	5.9	—	
												640-1170	.845	.270	(j)	Terminated	(2)
2-458[d]	200	100	40	20	1.5	5.4	CO-	72	230	210	1.0	620	.858	.833	4.0	(e)	
2-463	200	100	40	20	1.5	5.8	CO-	72	528	102	6	328	.903	.872	7.7	(e)	
2-476	200	100	40	20	2.5	8.2	CO-	72	390	50	12	114	.884	.490	(j)	Terminated	(2)
2-487	300	90	30	15	1.0	3.9	CO-	72	600	60	18	0- 400	.848	.836	1.5	—	
												400- 837	.836	.804	7.3	Terminated	(3)
2-484	300	90	30	15	1.5	4.7	CO-	72	600	60	18	911	.848	.792	5.8	Terminated	(1)
2-489	300	90	30	20	1.0	4.5	CO-	72	600	60	18	530	.831	.783	7.7	Terminated	(3)
2-491	300	90	30	20	1.5	5.6	CO-	72	600	60	18	426	.846	.822	4.6	Continuing	—
2-478	300	100	40	15	1.5	4.7	CO-	72	600	60	18	818	.882	.811	8.1	Terminated	(3)
2-474	300	100	40	15	1.5	4.7	CO-	72	600	60	18	647	.861	.801	9.5	Terminated	(3)
2-473	300	100	40	15	2.5	6.5	CO-	72	600	60	18	338	.846	.721	34	Terminated	(3)
2-458	300	100	40	20	1.5	5.4	CO-	72	345	315	1.0	428	.858	.804	12	(e)	
2-458[d]	300	100	40	20	1.5	6.4	CO-	72	600	60	18	292	.764	.718	20	Terminated	(3)
2-463[d]	300	100	40	20	1.5	5.8	CO-	72	600	60	18	294	.834	.796	14	Terminated	(3)
2-475	300	100	40	20	2.5	8.1	CO-	72	600	60	18	218	.773	.562	(j)	Terminated	(2)
TESTS WITH QUINTERRA ASBESTOS MATRIX																	
2-420	200	100	50	20	3.0	6.7	Counter	Dry	96	96	0.7	2000	.887	.820	3.4	Terminated	(4)(2)
2-425	200	100	50	21	3.0	6.7	Counter	Dry	96	96	0.7	0-1100	.894	.843	3.9		
												1100-2800	.843	.784	6.3	Terminated	(2)
2-421	300	100	50	20	3.0	6.8	Counter	Dry	144	144	0.8	0-1000	.842	.828	1.4		
												1000-2150	.828	.748	6.5	Terminated	(5)
2-446	400	100	40	20	2.0	5.1	CO-	72	460	420	1.0	0-1360	.848	.802	3.4		
												1360-2000	.802	.756	7.2		
												0-2000	.848	.756	4.5	Terminated	(2)
2-451	400	100	40	20	2.0	5.2	CO-	72	460	420	1.0	0-1300	.847	.788	4.5		
												1300-2000	.788	.732	8.0		
												0-2000	.847	.732	5.5	Terminated	(1)
2-445	400	100	50	20	2.0	5.4	CO-	55	480	440	1.0	1000	.824	.750	7.4	Terminated	(2)
2-444	400	100	50	20	2.0	5.3	CO-	61	1060	200	6	0- 200	.820	.802	11		
									1060	200	6	200- 310	.802	.772	(j)		
									480	440	1.0	310- 592	.772	.609	(j)	Terminated	(2)
2-433	400	100	50	20	3.0	6.5	Counter	55	480	440	1.0	512	.796	.764	(j)	Terminated	(2)

(Continued)

TABLE 3-2 (Continued)

TLT No.	Current Density (ma/cm²)	Temp. (°C)	Nominal KOH Conc. (%)	Matrix Thickness (Mils)	Initial KOH Loading: (g / g Matrix)	Initial KOH Loading: Total[a] In Cell (g)	H_2-O_2 Flow Direction	Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate (cc/min At 23°C & 0 Psig): H_2	Inlet Gas Flow Rate (cc/min At 23°C & 0 Psig): O_2	Exit H_2/O_2 Ratio	Test[b] Duration (Hours)	Working Voltage(v): Initial[c]	Working Voltage(v): Final[b]	Average[b] Voltage Decline Rate (mv/100 hours)	Status	Reason For Termination
TESTS WITH QUINTERRA ASBESTOS MATRIX (CONTINUED)																	
2-480	600	80	30	20	2.0	5.1	CO-	59	1230	90	38	430	.785	.732	12	Terminated	(3)
2-490	600	90	30	20	2.0	5.2	CO-	72	1230	90	38	503	.794	.743	11	Terminated	(3)
2-470	600	90	40→30	20	2.0→2.6	5.4	CO-	72	1230	90	38	690	.773	.717	8.1	Terminated	(6)(2)
2-457	600	100	35	20	2.0	5.1	CO-	81	690	630	1.0	304	.781	.726	19	(e)	
2-457[d]	400	100	35	20	2.0	5.1	CO-	81	460	420	1.0	320	.806	.780	4.4	Terminated	(7)
2-455	600	100	40	20	2.0	5.3	CO-	72	690	630	1.0	500	.797	.708	18	(e)	
2-455[d]	400	100	40	20	2.0	5.3	CO-	72	460	420	1.0	120	.784	.780	4.0[h]	(e)	
2-455[d]	600	100	40	20	2.0	5.3	CO-	72	1090	236	6	240	.675	.663	5.0	(e)	
2-455[d]	100	100	40	20	2.0	5.3	CO-	72	183	47	4.4	245	.936	.888	0	Terminated	(1)
2-465	600	100	40	20	2.0	5.3	CO-	72	1230	90	38	696	.804	.696	16	Terminated	(2)
2-468	600	100	40	20	2.0	5.3	CO-	H_2:67 O_2:81	1000	380	2.7	164	.742	.494	(j)	Terminated	(2)
2-469	600	100	40	20	2.0	5.2	CO-	H_2:67 O_2:81	1000	380	2.7	262	.761	.628	(j)	Terminated	(2)
TESTS WITH CERIA-PTFE MATRIX																	
2-494	200	100	50	25	~0.3[f]	~4.1[f]	CO-	55	240	220	1.0	232	.913	.877	2.6	Continuing	—
2-428	200	125	60	34	~0.4	~5.9	Counter	55	230	230	0.9	0- 930 930-1721	.935 .901	.901 .551	2.6 (j)	Terminated	(2)
2-430	200	125	60	32	~0.8	~6.7	Counter	55	230	230	0.9	0- 230 230- 470(g)	.932 .908	.908 .906(g)	13 0.9(g)	Terminated	(5)
2-449	300	125	55	30	~1.1	~8.3	CO-	72	360	330	1.0	138	.846	.710	(j)	Terminated	(2)
2-454	300	125	55	34	~1.2	~8.6	CO-	72	360	330	1.0	580	.862	.797	7	Terminated	(2)
2-460	300	125	55	34	~1.2	~9.2	CO-	72	360	330	1.0	716[h]	.866	.780[h]	7[h]	Terminated	(1)
2-434	300	125	60	30	~0.7	~6.2	Counter	55	345	345	0.9	700	.894	.841	6.4	Terminated	(8)(9)(2)
2-435	300	125	60	26	~0.5	~5.5	Counter	55	345	345	0.9	406	.902	.872	6.1	Terminated	(8)(9)(2)
2-448	300	125	60	23	~1.0	~7.6	CO-	55	345	345	0.9	544	.880	.837	6.0	Terminated	(8)(9)(2)
2-447	300	125	60 58	23	~1.0	~6.7	CO-	61 61	800 360	150 330	6 1.0	0- 140 140- 420	.903 .875	.875 .852	20 5.0	Terminated	(8)(9)(2)
2-441	100	150	67	30	~0.7	~7.3	Counter	55	115	115	0.9	402	1.011	.975	5.5	Terminated	(8)(9)(2)
TESTS WITH CERIA-PTFE-PCTFE MATRIX																	
			(g)		(f)(i)	(f)(i)											
2-466	200	125	30→50	20	~1.1→0.6	~5.0→3.0	CO-	72	73	53	1.0	65	.907	.863	70	Terminated	(8)(9)(2)
2-471	200	125	40→50	20	~1.1→0.9	~5.3→4.2	CO-	72	73	53	1.0	94	.942	.896	35	Terminated	(8)(9)(2)
2-472	200	125	40→50	—	~1.1→0.9	~4.8→3.9	CO-	72	73	53	1.0	8	.901	0	—	Terminated	(8)(9)(2)
2-481	200	125	40→50	22	~1.2→1.0	~5.7→4.8	CO-	72	73	53	1.0	300	.902	.880	6.1	Terminated	(8)(9)(2)
2-482	200	125	40→50	20	~1.3→1.0	~6.0→5.0	CO-	72	73	53	1.0	300	.895	.860	12	Terminated	(8)(9)(2)
2-483	100	150	67	26	~1.8	~5.8	Counter	55	115	115	0.9	120	1.022	.990	8	Terminated	(8)(9)(2)
TESTS WITH POTASSIUM TITANATE-PTFE MATRIX																	
2-495	200	125	30→50	28	1.3→0.7	5.5→2.8	CO-	72	73	53	1.0	56	.684	.682	—	Continuing	—

(Continued)

TABLE 3-2 (CONTINUED)

Letter Key

(a) Of the total electrolyte in the cell, 35-40% was generally introduced in the electrodes prior to cell assembly.
(b) Prior to any accelerated or abrupt voltage decline.
(c) Maximum voltage within first 100 hours.
(d) Test was previously run at a different current density as shown in Table.
(e) Test continued at different current density as shown in Table.
(f) Ceria-PTFE, Ceria-PTFE-PCTFE and Potassium Titanate-PTFE matrices are kept equilibrated with water and then electrolyte before test - Accordingly loadings shown are approximate and are calculated from average values of 1.5, 0.95 and 0.7 g dry matrix/cc water-wet matrix respectively.
(g) Prior to temporary drop in cell temperature to 110°C.
(h) Prior to formation of plug in hydrogen saturator.
(i) In order to reduce the initial loading 30-40%, KOH was loaded into cell and then concentrated to 50%.
(j) Accelerated voltage decline.

Reasons for Termination

(1) Voltage decline rate defined.
(2) Accelerated voltage decline.
(3) High voltage decline rate.
(4) Caustic from scrubbers foamed over.
(5) Voltage erratic.
(6) Air accidentally introduced into anode.
(7) Current could not be reached at minimum load resistance.
(8) Matrix broke.
(9) Gas cross-leak.

TABLE 3-3

KOH CONCENTRATION GRADIENT

TLT No.	Matrix	Current Density (ma/cm²)	Temp. (°C)	Nominal KOH Conc. (%)	Inlet Gas Dew Point (°C)	Elapsed Time (Hours)	Equilibrium KOH Conc. (%) At: H_2 Exit	Equilibrium KOH Conc. (%) At: O_2 Exit	KOH Conc. Gradient (%)	Average KOH Conc. Gradient (%)
2-357	ACCO-I Asbestos	100	100	50	45	4195	50.5	49	- 1.5	- 0.2
						4414	48.5	49.5	1.0	
2-324	Fuel Cell Asbestos	100	100	50	45	5730	50	48	- 2.0	- 2.6[a]
						5925	50	48	- 2.0	
						6599	50	48	- 2.0	
						7070	51	48	- 3.0	
						7221	49	47	- 2.0	
						7557	49	45	- 4.0	
						8613	51	48	- 3.0	
						9408	43.5	48	4.5	4.5[a]
2-479	Fuel Cell Asbestos	200	93	35	70	19	37	38	1.0	1.2
						647	37	39.5	2.5	
2-477	Fuel Cell Asbestos	200	100	40	72	18	42	42	0	1.2
						815	41.5	43	1.5	
2-458	Fuel Cell Asbestos	200	100	40	72	428	39	42.5	3.5	3.5
2-463	Fuel Cell Asbestos	200	100	40	72	20	42.5	43.5	1.0	1.2
						44	42.5	44	1.5	
2-476	Fuel Cell Asbestos	200	100	40	72	21	41.5	47	5.5	5.5
2-487	Fuel Cell Asbestos	300	90	30	72	600	33	35	2.0	2.0
2-484	Fuel Cell Asbestos	300	90	30	72	696	34.5	37	2.5	2.5
2-489	Fuel Cell Asbestos	300	90	30	72	600	32	40	8.0	8.0
2-491	Fuel Cell Asbestos	300	90	30	72	168	32.5	31.5	- 1.0	- 1.0
2-478	Fuel Cell Asbestos	300	100	40	72	23	42.5	43.5	1.0	0.2
						676	42.0	41.5	- 0.5	
2-473	Fuel Cell Asbestos	300	100	40	72	49	42	44.5	2.5	2.5
2-458	Fuel Cell Asbestos	300	100	40	72	39	38	43.5	5.5	5.2
						354	38.5	43.5	5.0	
2-463	Fuel Cell Asbestos	300	100	40	72	174	41.5	43	1.5	1.5
2-475	Fuel Cell Asbestos	300	100	40	72	94	41	44	3.0	3.0
2-420	Quinterra Asbestos	200	100	50	Dry	1678	43.5	52.5	9.0	8.2
						1704	44	53	9.0	
						1895	44	53	9.0	
						2180	45	51	6.0	
2-425	Quinterra Asbestos	200	100	50	Dry	1385	44.5	54.5	10.0	8.8
						1559	44	52	8.0	
						1844	45	50.5	5.5	
						2255	45	52.5	7.5	
						2683	43.5	53.5	10.0	
						2855	43.5	54	10.5	
						3191	44	54	10.0	
2-421	Quinterra Asbestos	300	100	50	Dry	1653	43	53.5	10.5	9.7
						1844	44.5	53.5	9.0	
						2129	45	54.5	9.5	
2-446	Quinterra Asbestos	400	100	40	72	19	40	44	4.0	3.5
						186	41.5	45	3.5	
						357	40	44.5	4.5	
						815	40	43.5	3.5	
						983	40.5	43.5	3.0	
						1296	41.5	44	2.5	
						1798	40	43.5	3.5	
2-451	Quinterra Asbestos	400	100	40	72	18	41	44.5	3.5	3.1
						21	41	44.5	3.5	
						359	40.5	44	3.5	
						525	40.5	44	3.5	
						840	41.5	44	2.5	
						1343	41	44	3.0	
						1725	40.5	43.5	3.0	
						1917	41	43.5	2.5	

Continued

TABLE 3-3 (Continued)

Test No.	Matrix	Current Density (ma/cm²)	Temp. (°C)	Nominal KOH Conc. (%)	Inlet Gas Dew Point (°C)	Elapsed Time (Hours)	Equilibrium KOH Conc. (%) At: H_2 Exit	Equilibrium KOH Conc. (%) At: O_2 Exit	KOH Conc. Gradient (%)	Average KOH Conc. Gradient (%)
2-445	Quinterra Asbestos	400	100	50	55	44	46	50.5	4.5	3.0
						221	46	50.5	4.5	
						380	46.5	49.5	3.0	
						839	48	50.5	2.5	
						1008	48	50	2.0	
						1317	48.5	50	1.5	
2-433	Quinterra Asbestos	400	100	50	55	360	47	52	5.0	4.5
						383	48	52	4.0	
2-444	Quinterra Asbestos	400	100	50	61	19	46	50.5	4.5	3.9
						67	46	49.5	3.5	
						235	46.5	49.5	3.0	
						404	44	48.5	4.5	
2-480	Quinterra Asbestos	600	80	30	59	96	31.5	32.5	1.0	1.2
						311	32	33.5	1.5	
2-490	Quinterra Asbestos	600	90	30	72	287	32	36.5	4.5	4.5
2-470	Quinterra Asbestos	600	90	30	72	212	32.5	35	2.5	2.0
						696	33	34.5	1.5	
2-455	Quinterra Asbestos	600	100	40	72	45	38.5	44	5.5	5.8[a]
						139	38.5	43.5	5.0	
						309	37	44	7.0	
						1123	42.5	43.5	1.0	1.0[a]
2-465	Quinterra Asbestos	600	100	40	72	115	42	44.5	2.5	2.5
						502	42	44.5	2.5	
2-469	Quinterra Asbestos	600	100	40	H_2 : 67 O_2 : 81	142	41.5	42	0.5	0.5
2-428	Ceria-PTFE	200	125	60	55	1049	56.5	60	3.5	4.0
						1223	56	60.5	4.5	
2-430	Ceria-PTFE	200	125	60	55	671	56	60	4.0	4.0
2-454	Ceria-PTFE	300	125	55	72	45	52.5	54.5	2.0	2.0[a]
						187	55	55.5	0.5	
						357	52.5	55.5	3.0	
						691	53	55.5	2.5	
						853	53.5	51.5	- 2.0	- 2.0[a]
2-460	Ceria-PTFE	300	125	55	72	39	52.5	55.5	3.0	3.0
						288	52.5	55.5	3.0	
2-434	Ceria-PTFE	300	125	60	55	332	55.5	61	5.5	5.2
						534	55.5	60.5	5.0	
2-435	Ceria-PTFE	300	125	60	55	145	56	61.5	5.5	5.2
						338	56	61	5.0	
2-448	Ceria-PTFE	300	125	60	55	19	56	61	5.0	4.8
						168	56	60.5	4.5	
						620	56	61	5.0	
2-447	Ceria-PTFE	300	125	60 58	61	44	56.5	59.5	3.0	3.7
						215	54.5	58.5	4.0	
						672	54.5	58.5	4.0	
2-441	Ceria-PTFE	100	150	67	55	21	65.5	69	3.5	1.3
						240	65.5	65.5	0	
						332	68	68.5	0.5	
2-466	Ceria-PTFE-PCTFE	200	125	50	72	22	48.5	48.5	0	0
2-481	Ceria-PTFE-PCTFE	200	125	50	72	191	46.5	49.5	1.0	1.0
2-482	Ceria-PTFE-PCTFE	200	125	50	72	144	49	50	1.0	1.0
2-483	Ceria-PTFE-PCTFE	100	150	67	55	28	68	68	0	0

(a) Gradient and decline rate during period indicated in brackets.

TABLE 3-4

CONVERSION OF KOH TO K_2CO_3 AND PERFORMANCE STABILITY

Test	Current Density (ma/cm^2)	Matrix	Duration Of Stable Performance (Hours)	Total Gas Flow (Liters)	Estimated[(a)] KOH Conversion (%)
2-324	100	Fuel Cell Asbestos	9700	86,000	28
2-458	200	Fuel Cell Asbestos	620[(b)]	33,400	15
2-446	400	Quinterra Asbestos	1360	71,600	15

(a) Estimated from Figure 3-16.

(b) Test 2-458 first ran at 300 ma/cm^2 for 428 hours.

TABLE 3-5

AVERAGE CRYSTALLITE SIZE OF LIFE-TESTED ELECTRODES

Test	Temp. (°C)	Current Density (ma/cm^2)	Test Duration (Hours)	Average Crystallite[a] Size (Å) Of: Anode	Cathode
Fresh Electrodes	---	---	-----	95	95
2-357	100	100	5,007	115	105
2-324	100	100	10,247	—	90
2-476	100	200	114	110	125
2-477	100	200	1,170	—	120
2-425	100	200	3,330	150	155
2-491	90	300	426	100	120
2-484	90	300	911	160	165
2-475	100	300	218	120	120
2-478	100	300	818	115	115
2-421	100	300	2,150	135	150
2-433	100	400	512	135	155
2-445	100	400	1,481	85	130
2-451	100	400	2,009	95	145
2-446	100	400	2,132	90	160
2-480	80	600	430	—	115
2-470	90	600	1,058	115	115
2-468	100	600	164	100	130
2-465	100	600	696	110	150
2-430	125	200	808	160	140
2-428	125	200	1,721	160	165
2-449	125	300	138	105	120
2-435	125	300	599	135	155
2-483	150	100	168	135	110
2-441	150	100	474	140	135
2-423[b]	150	200	256	120	140

(a) Measured on electrode face adjacent to matrix.
(b) Reported previously.[2]

LOSS OF MATRIX AREA IN 60% KOH AT 125°C

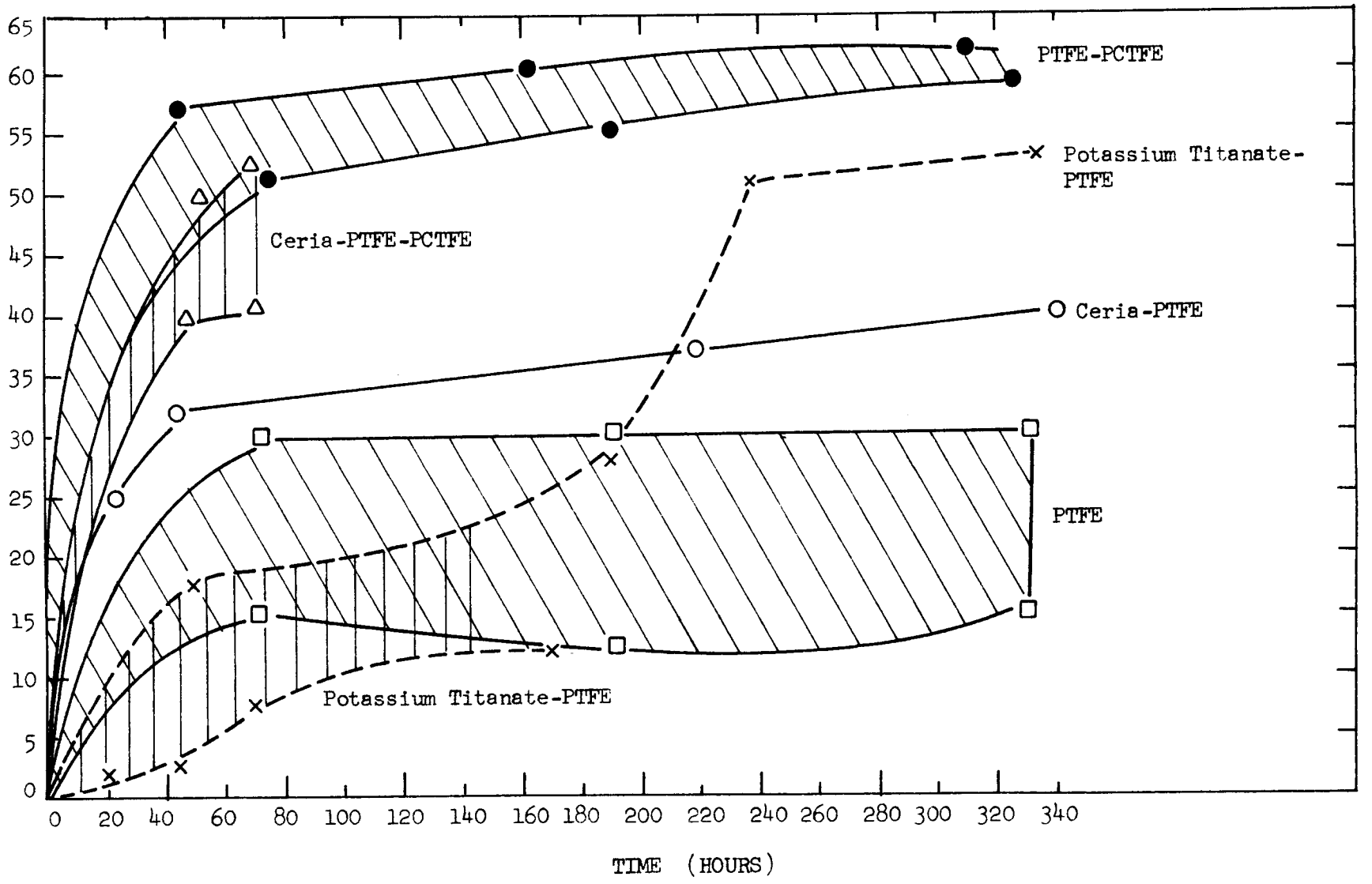


Figure 3-1

SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE
ACCO I ASBESTOS MATRIX: 100°C: 100 ma/cm²

KOH Conc.: 50%

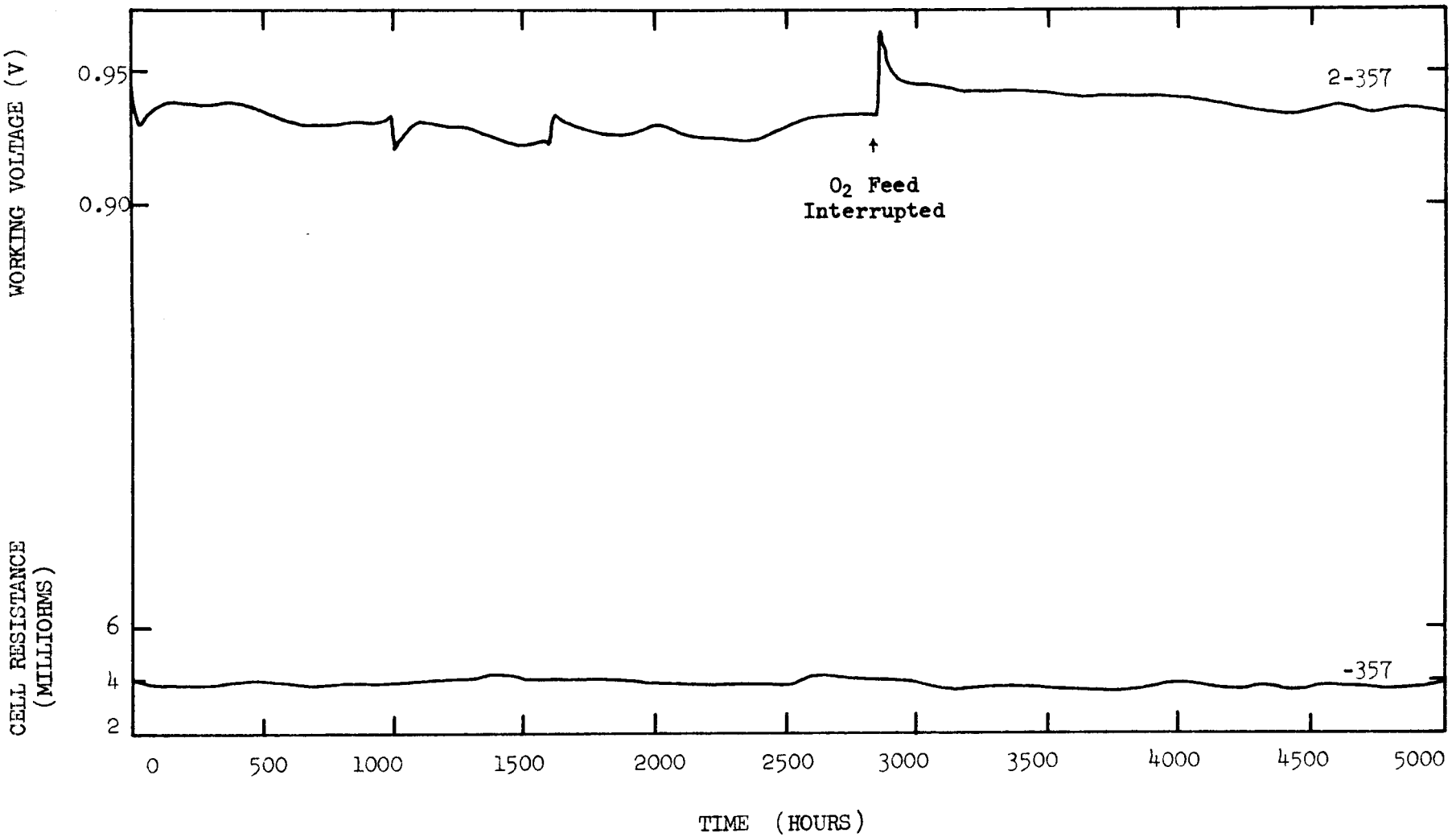


Figure 3-2

SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 100°C: 100 ma/cm²

KOH Conc.: 50%

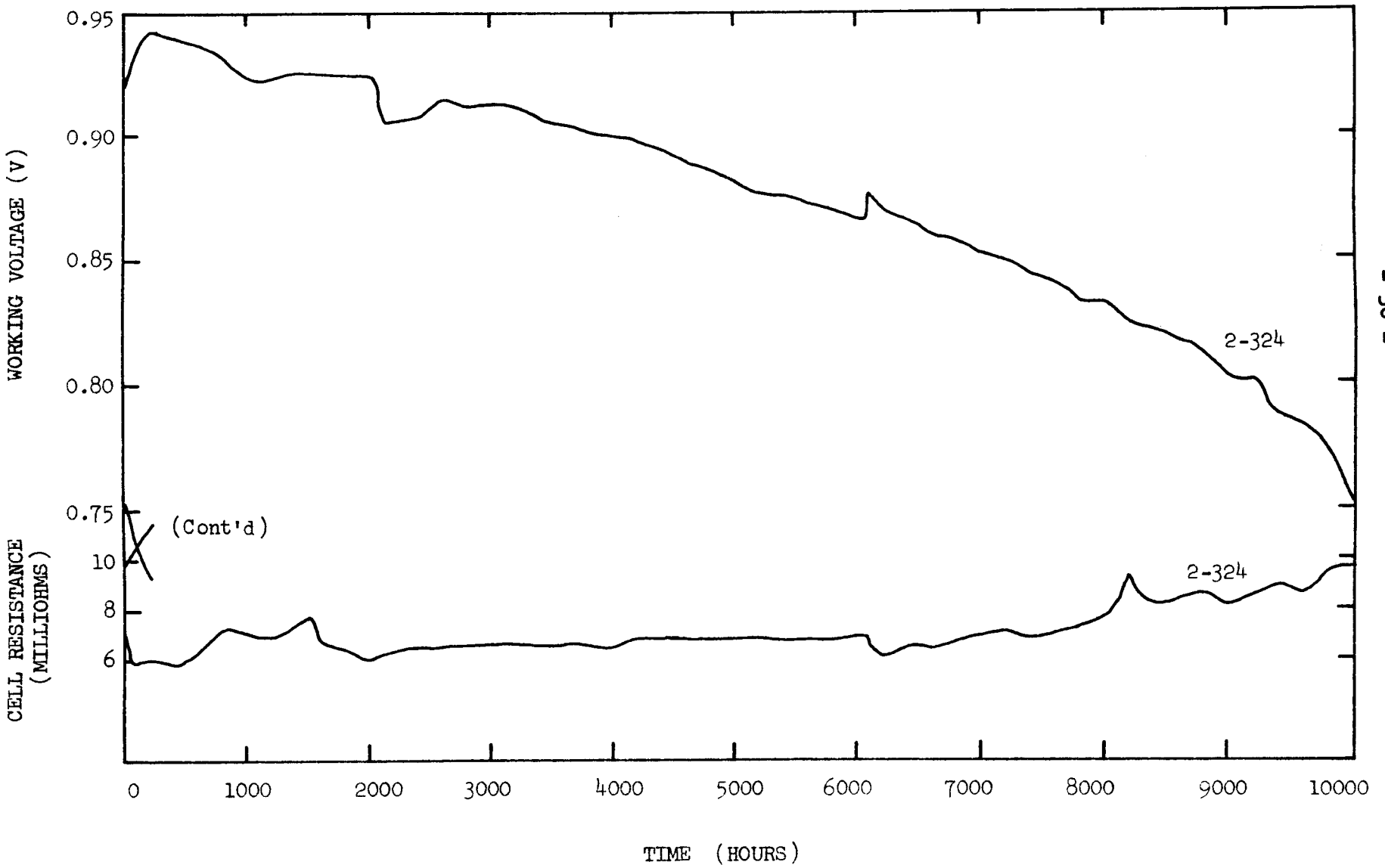


Figure 3-3

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 93-100°C: 200 ma/cm²

93°C: 35% KOH: 2-479
100°C: 40% KOH: 2-477, 2-458, 2-463

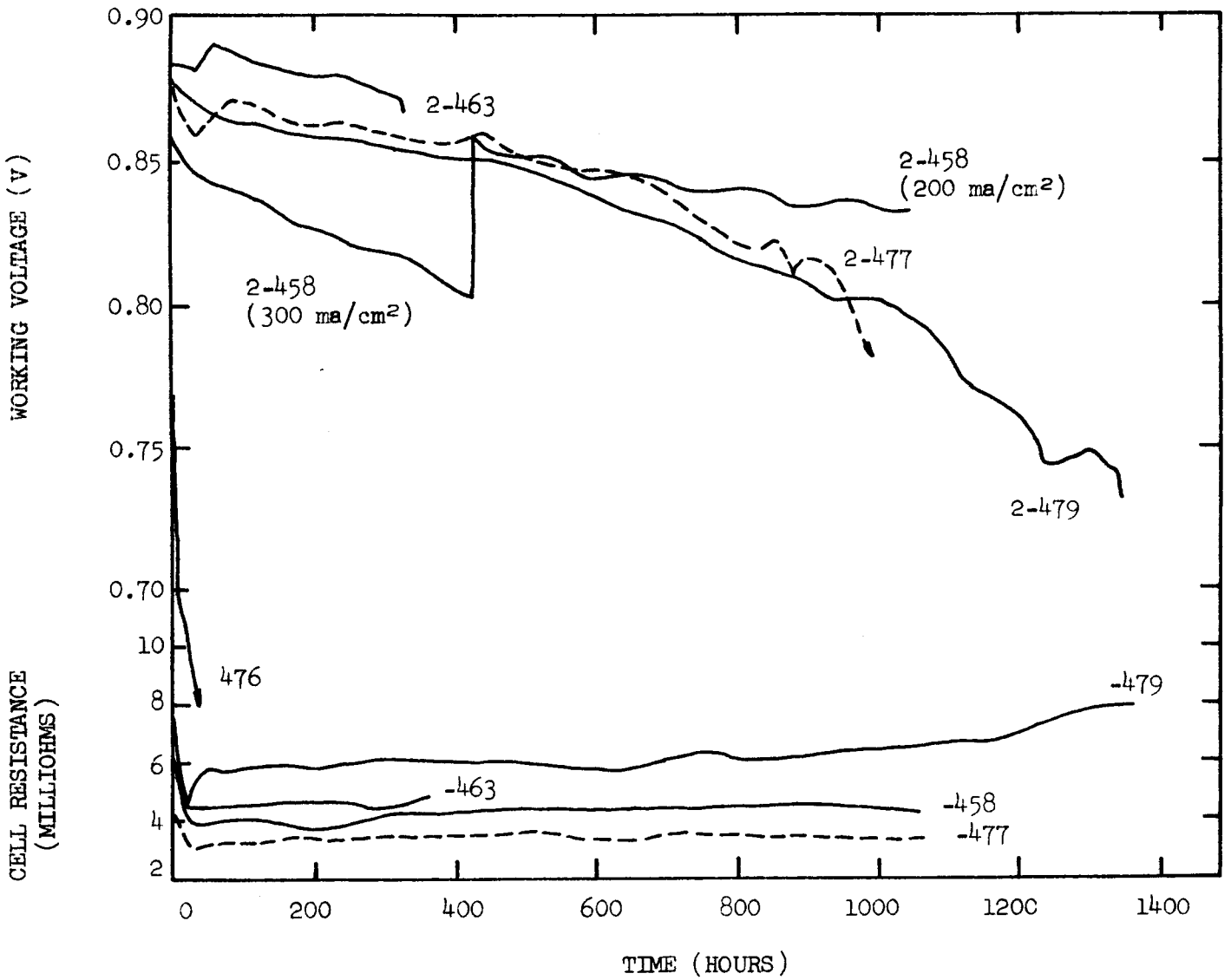


Figure 3-4

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 90-100°C: 300 ma/cm²

Matrix Thickness: 15 Mils
90°C: 30% KOH: 2-484, 2-487
100°C: 40% KOH: 2-473, 2-474, 2-478

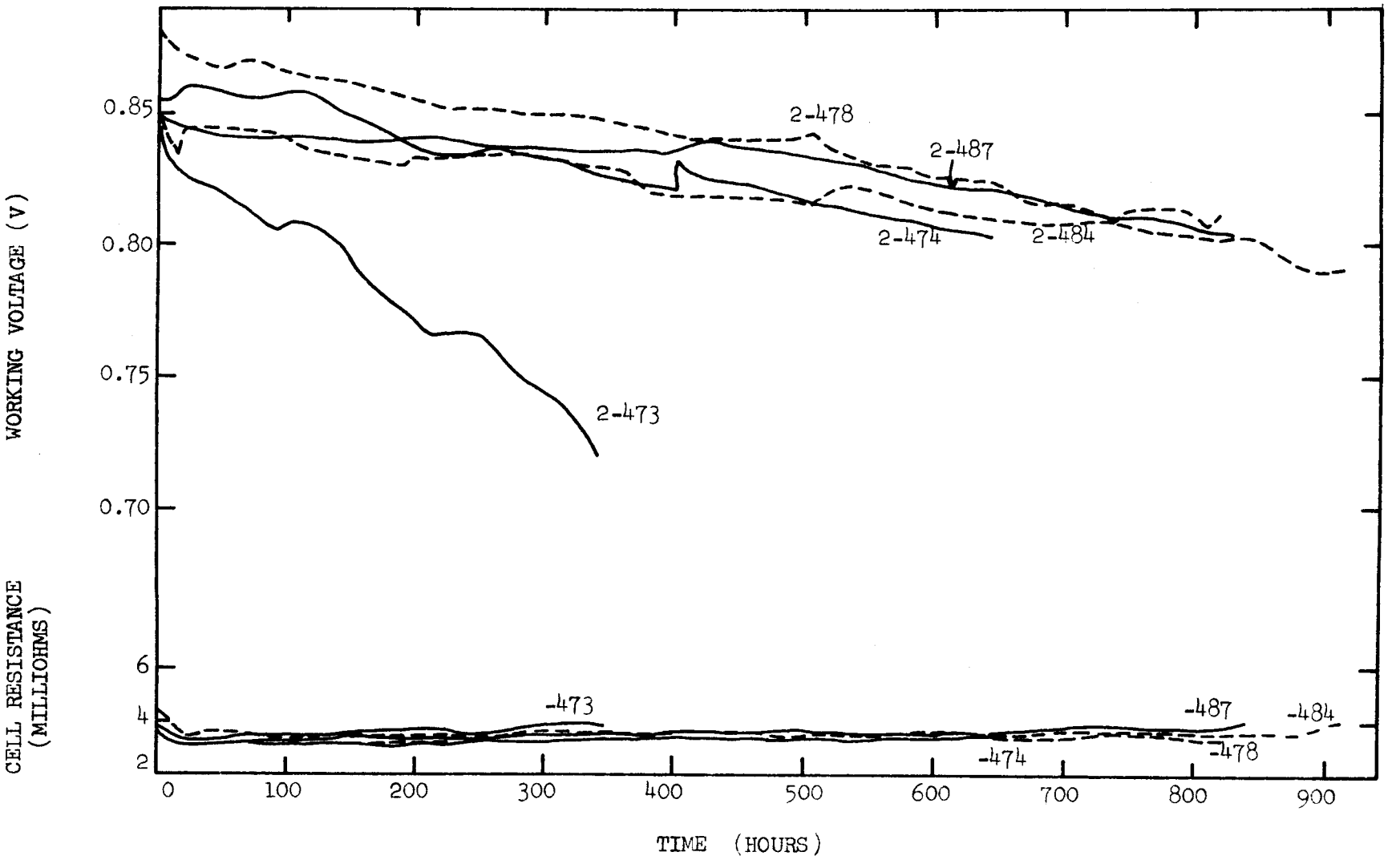


Figure 3-5

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
FUEL CELL ASBESTOS MATRIX: 90-100°C: 300 ma/cm²

Matrix Thickness: 20 Mils
90°C: 30% KOH: 2-489, 2-491
100°C: 40% KOH: 2-458, 2-475

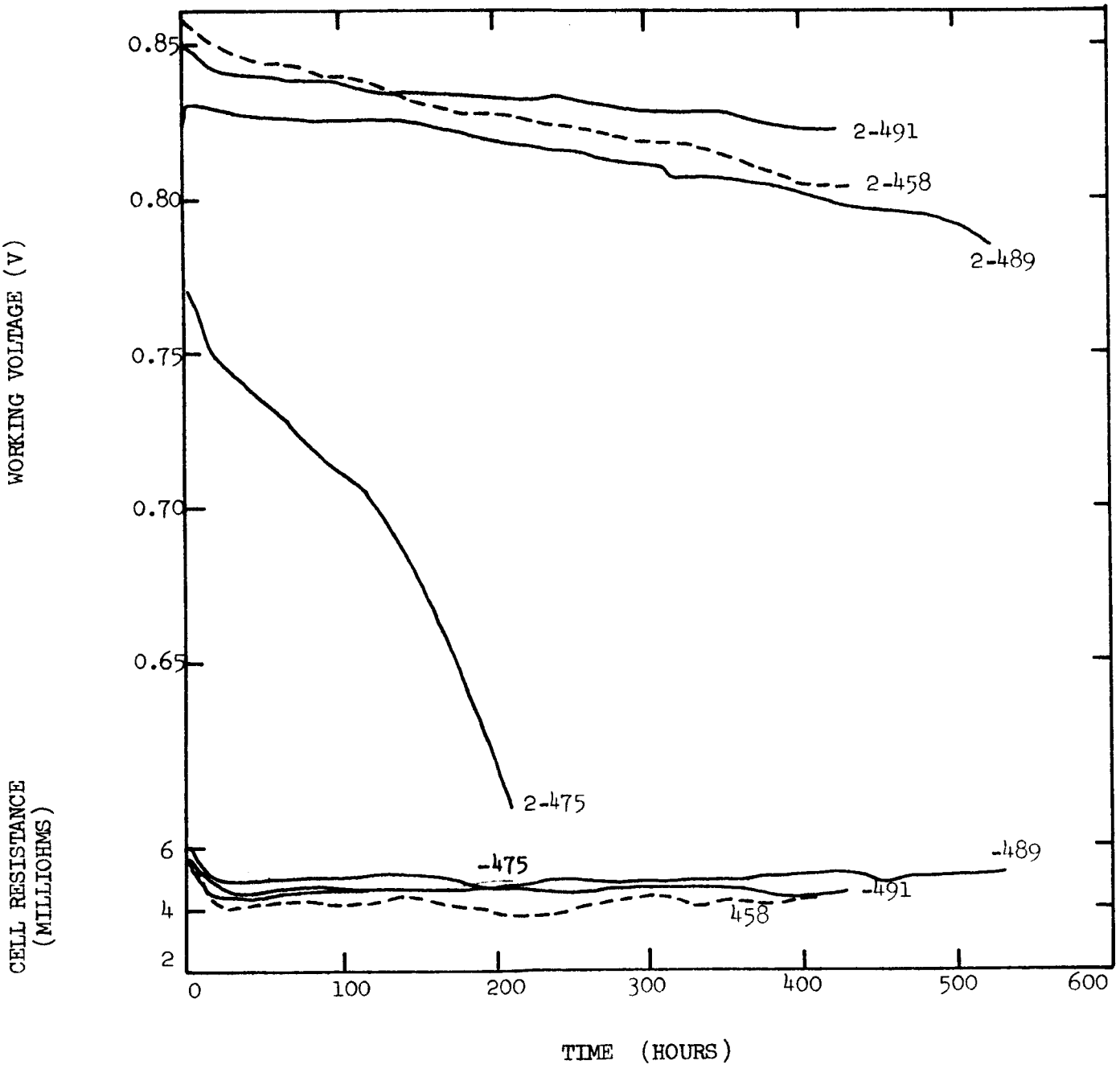


Figure 3-6

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 100°C: 200-300 ma/cm²

KOH Conc.: 50%
200 ma/cm²: 2-420, 2-425
300 ma/cm²: 2-421

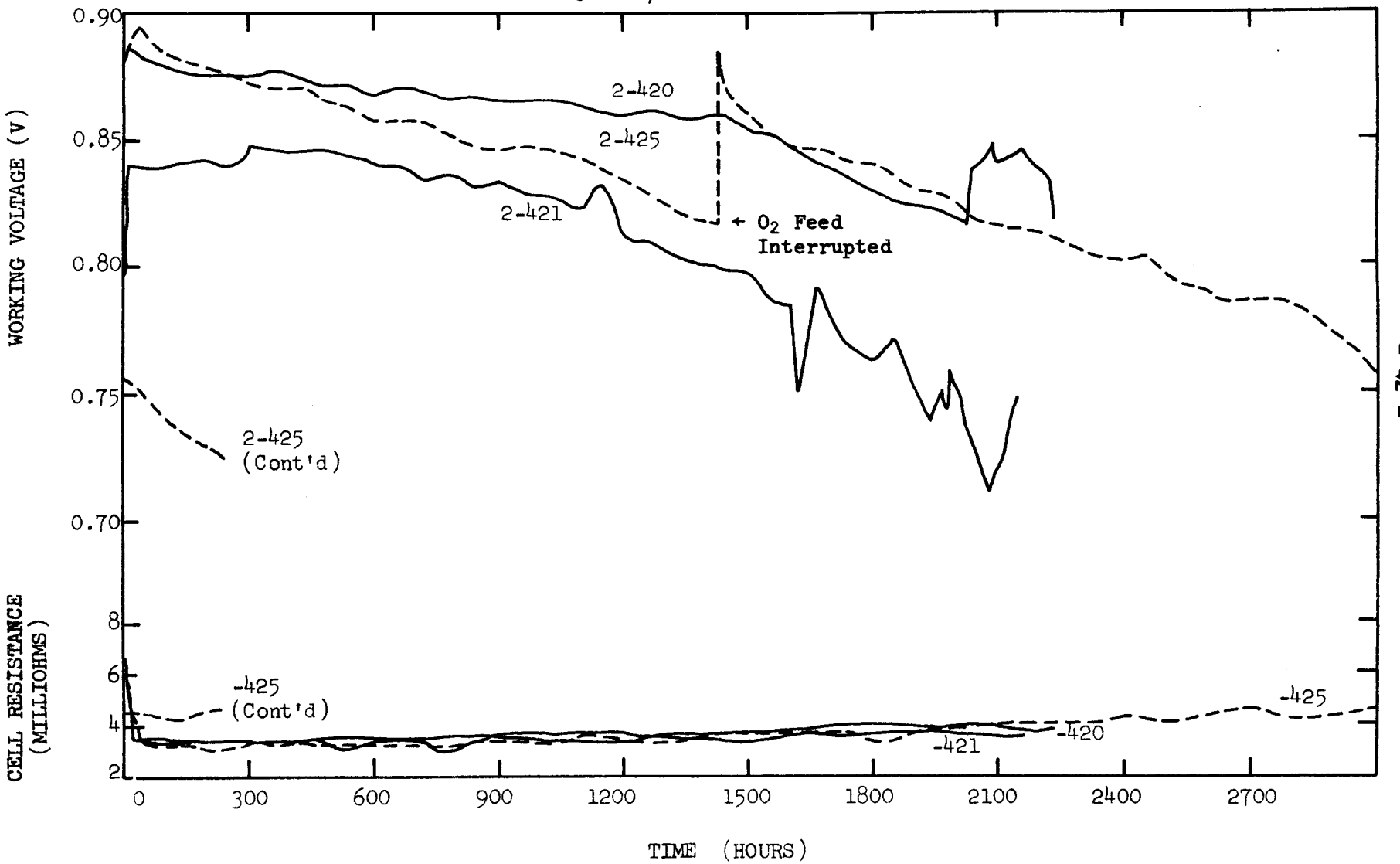


Figure 3-7

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 100°C: 400 ma/cm²

40% KOH: 2-446, 2-451
50% KOH: 2-433, 2-444, 2-445

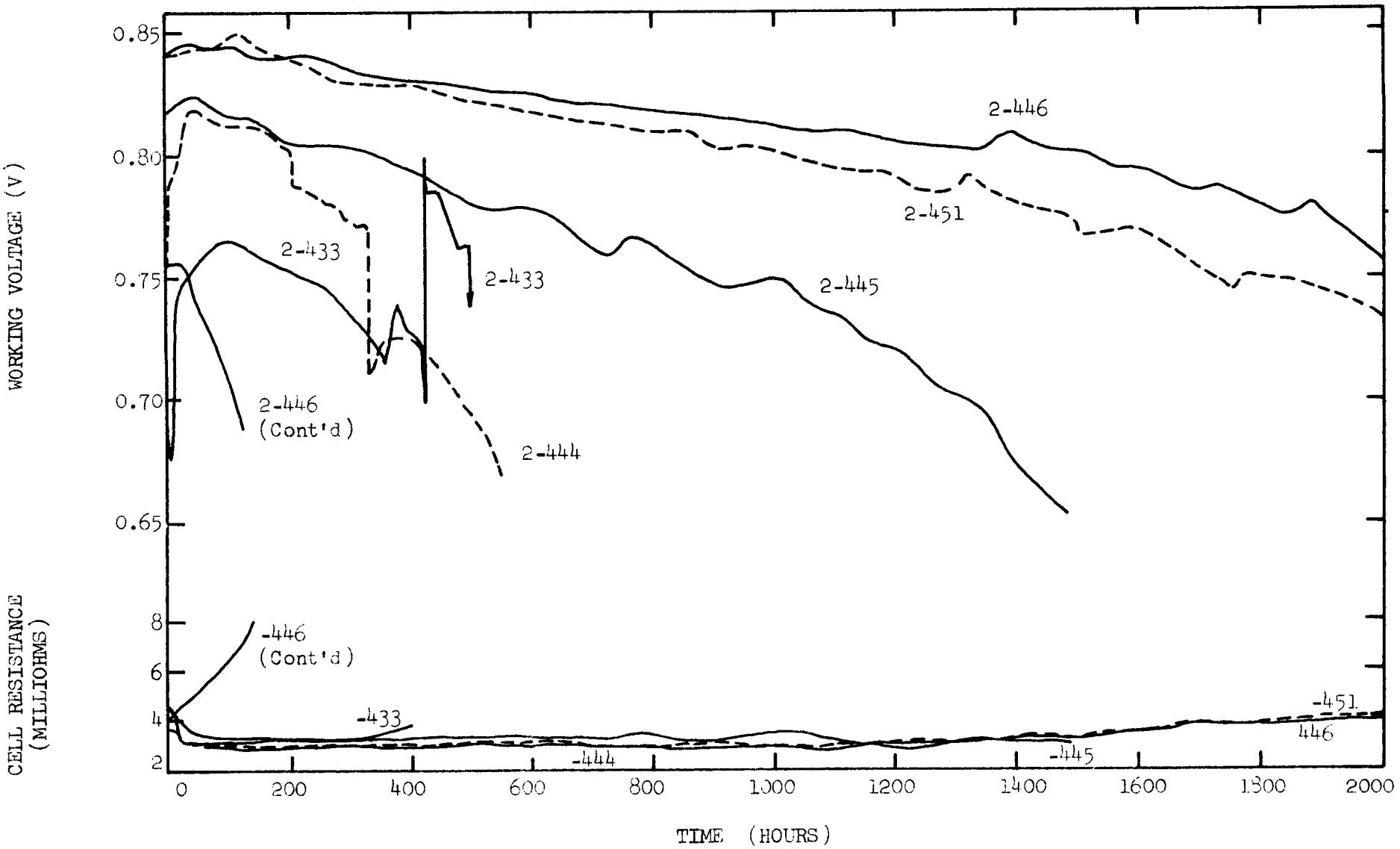


Figure 3-8

SMALL CELL TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 100°C: 600, 400 & 100 ma/cm²

35% KOH: 2-457
40% KOH: 2-455

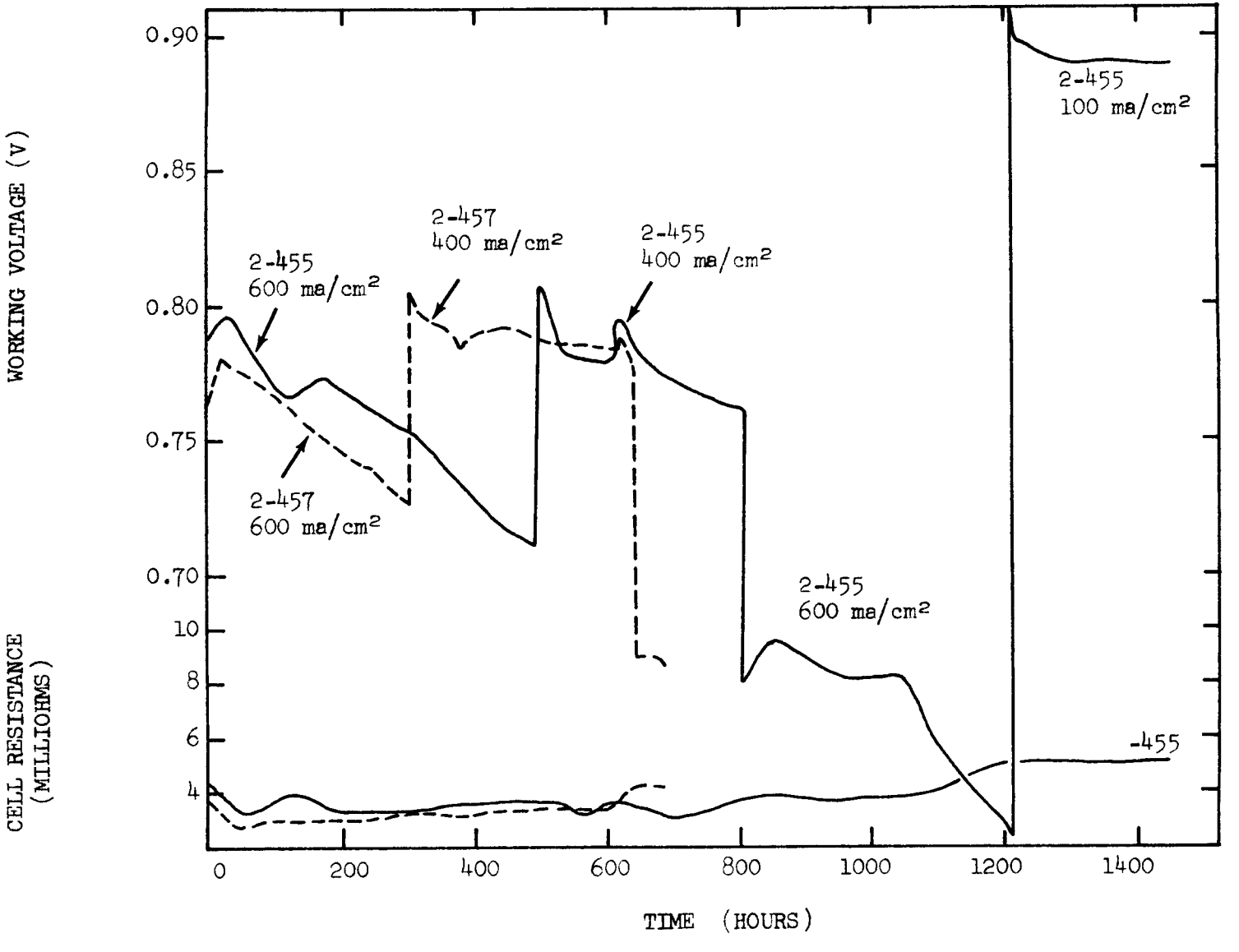


Figure 3-9

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 80-100°C: 600 ma/cm²

80°C: 30% KOH: 2-480
90°C: 30% KOH: 2-490
100°C: 40% KOH: 2-465, 2-468, 2-469

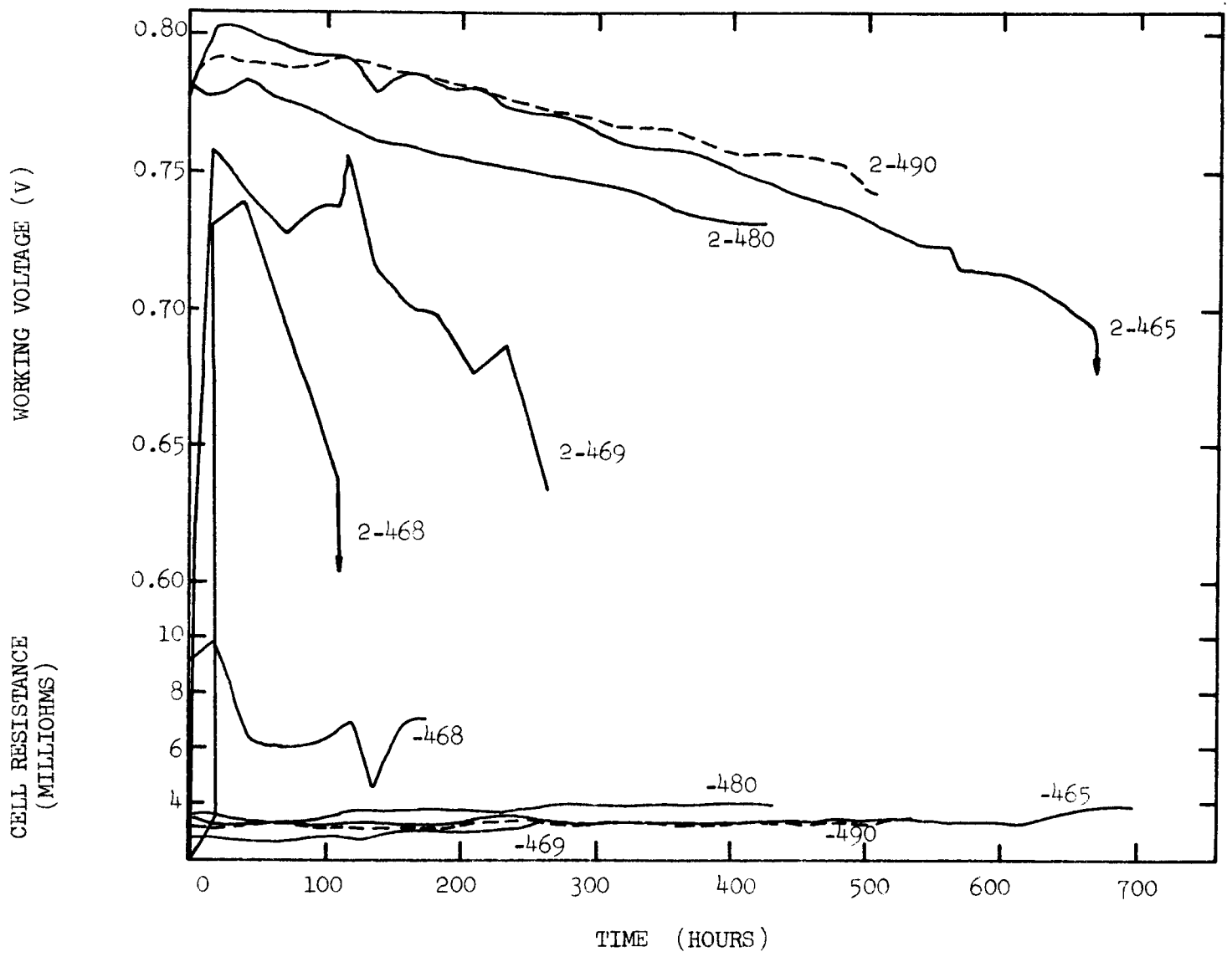


Figure 3-10

SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE
QUINTERRA ASBESTOS MATRIX: 90°C: 600 ma/cm²

KOH Conc.: 30%

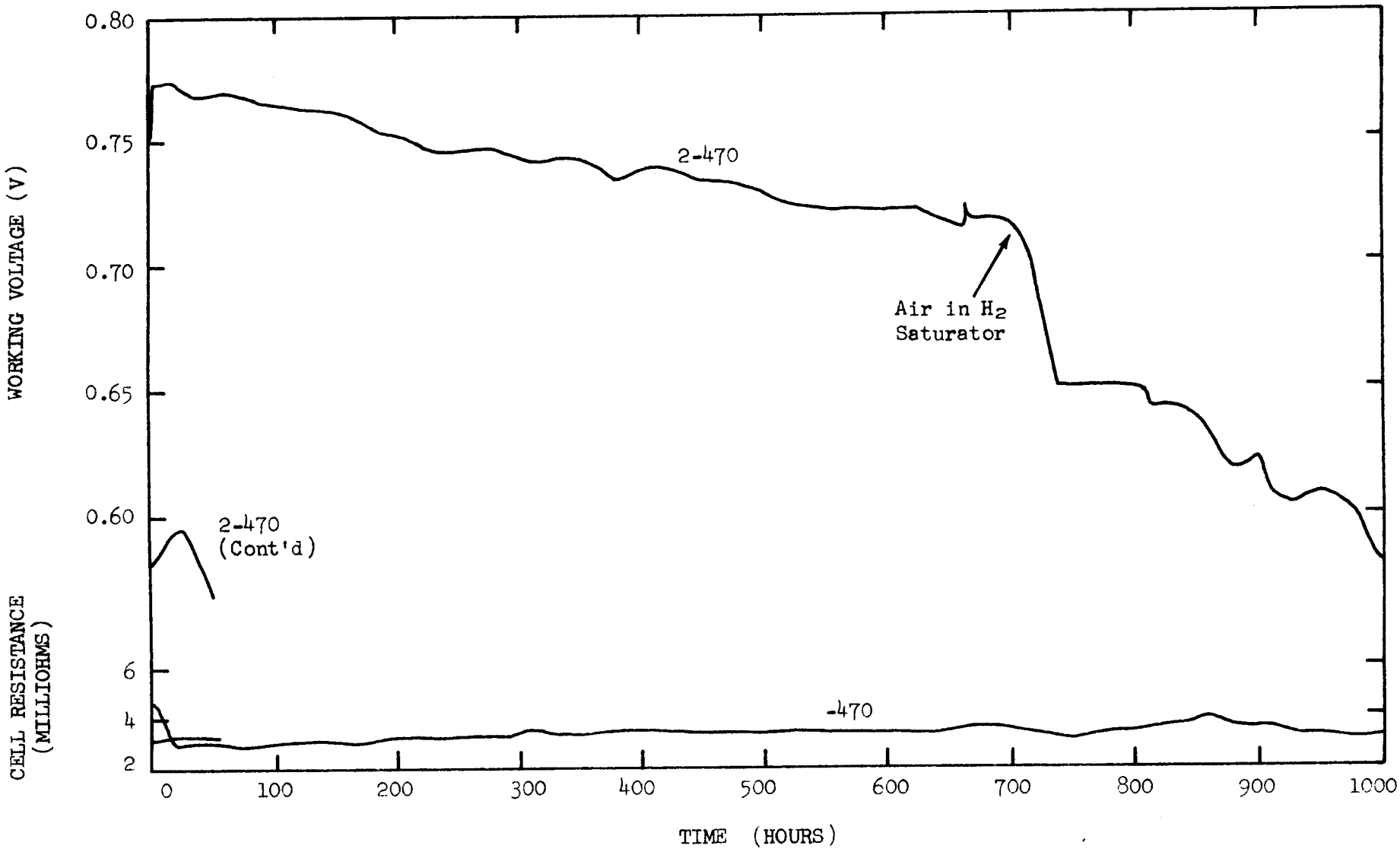


Figure 3-11

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
CERIA-PTFE MATRIX: 100-125°C: 200 ma/cm²

100°C: 50% KOH: 2-494
125°C: 60% KOH: 2-428, 2-430

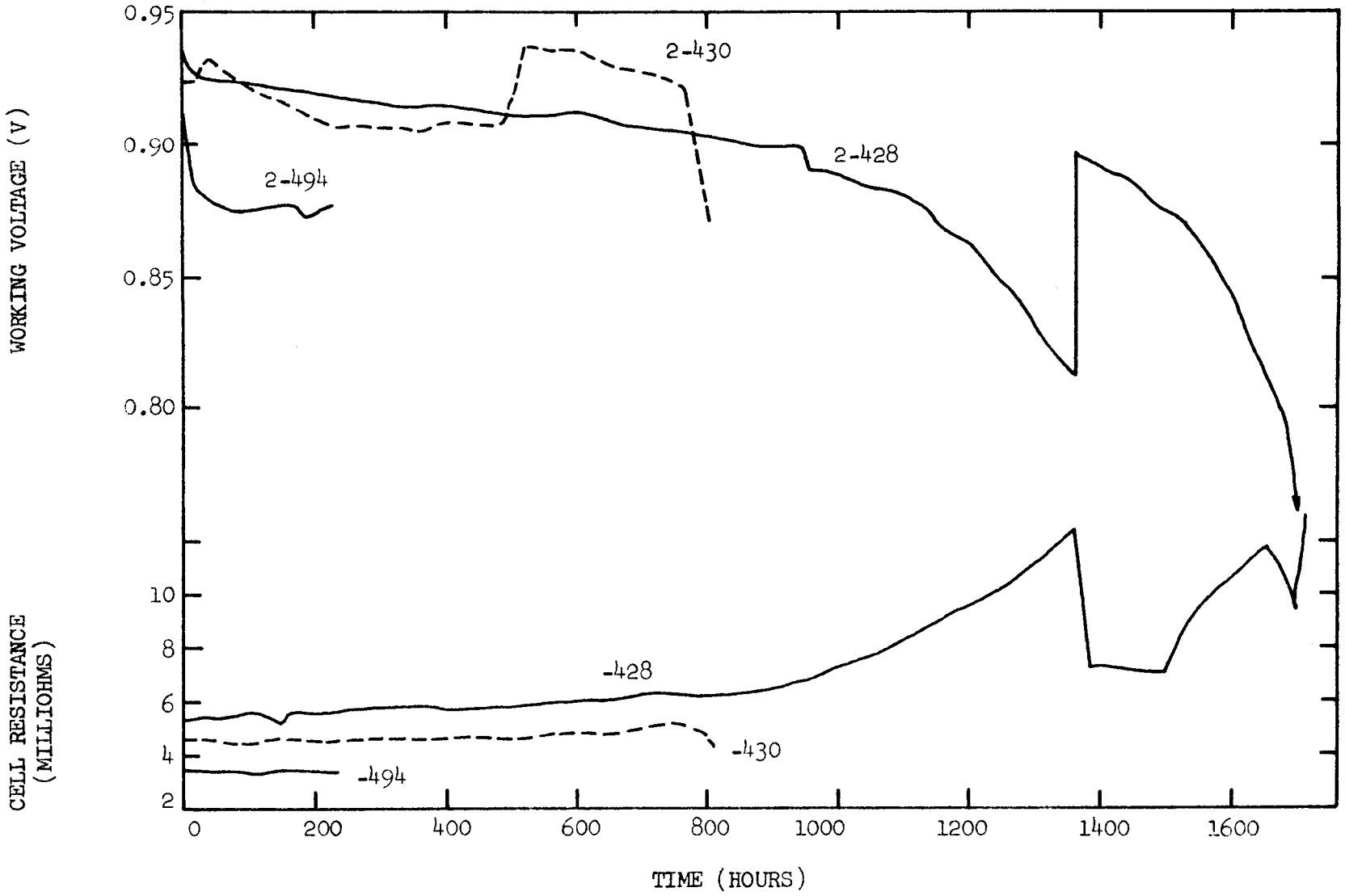


Figure 3-12

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
CERIA-PTFE MATRIX: 125°C: 300 ma/cm²

55% KOH: 2-449, 2-454, 2-460
60% KOH: 2-434, 2-435, 2-447, 2-448

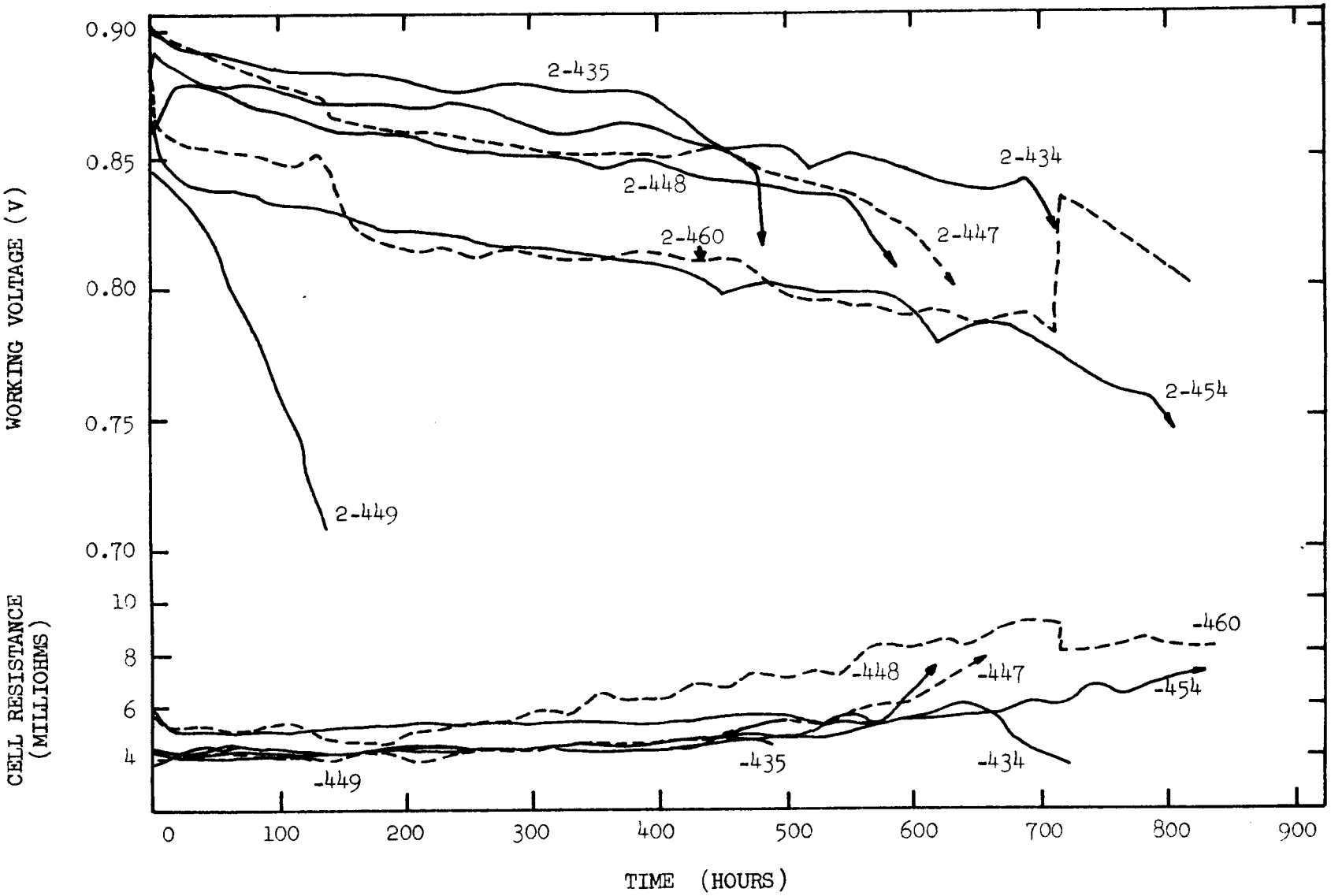


Figure 3-13

SMALL CELL LIFE TEST AT ATMOSPHERIC PRESSURE
CERIA-PTFE MATRIX: 150°C: 100 ma/cm²

KOH Conc.: 67%

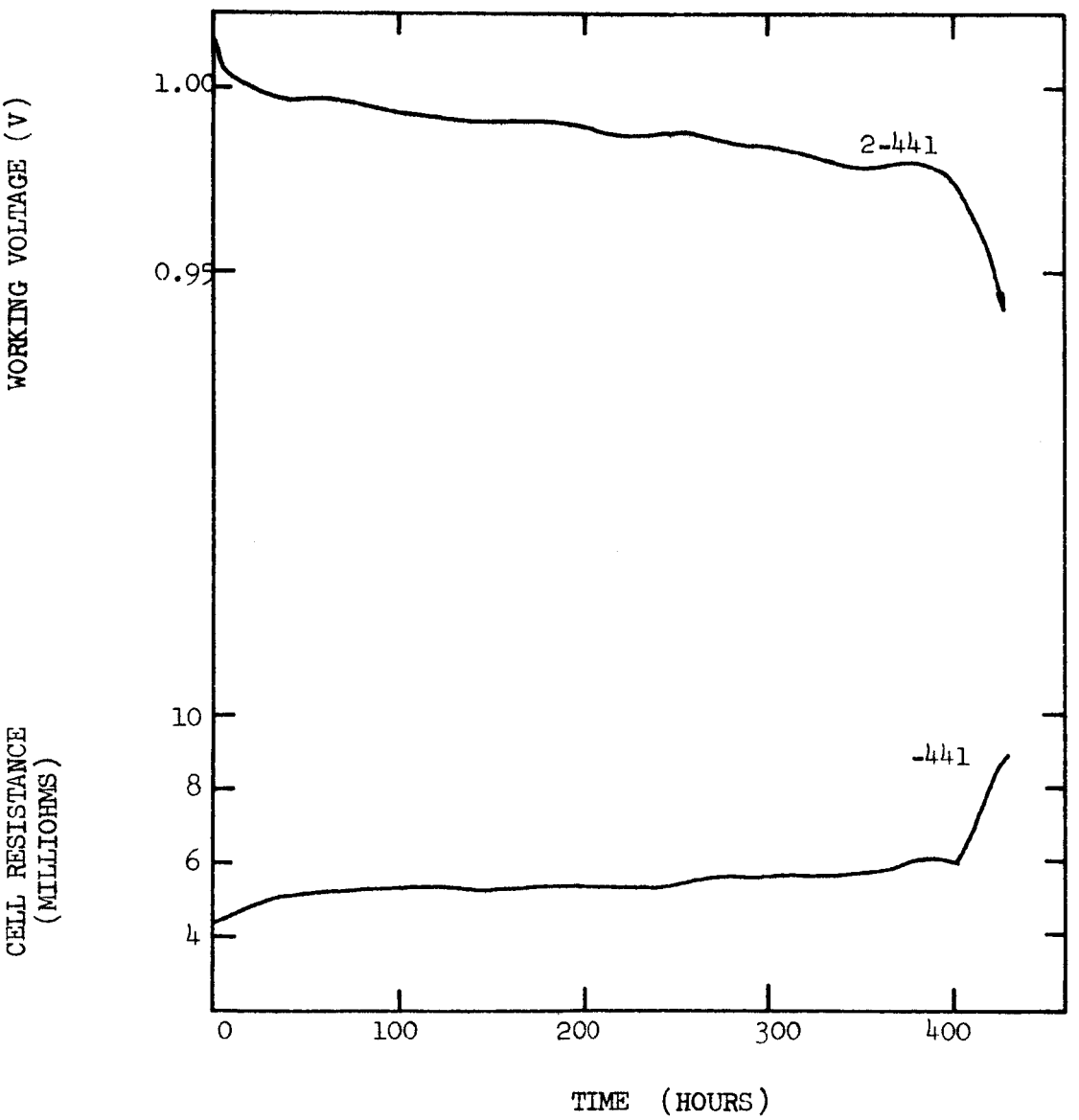


Figure 3-14

SMALL CELL LIFE TESTS AT ATMOSPHERIC PRESSURE
CERIA-PTFE-PCTFE MATRIX: 125-150°C: 100-200 ma/cm²

125°C: 200 ma/cm²: 50% KOH: 2-466, 2-471, 2-481, 2-482
150°C: 100 ma/cm²: 67% KOH: 2-483

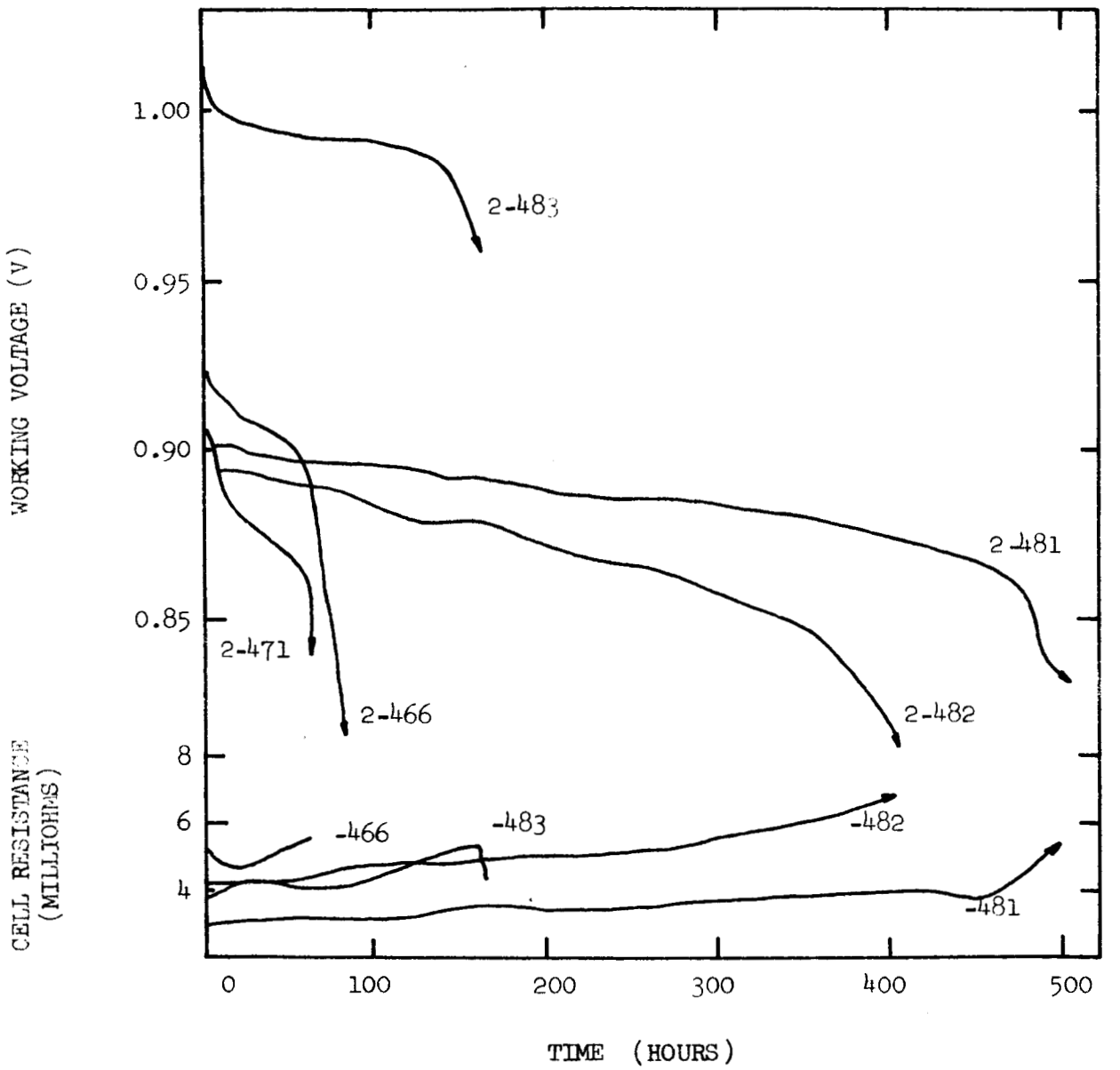


Figure 3-15

CONVERSION OF KOH TO K_2CO_3 DURING LIFE TESTS

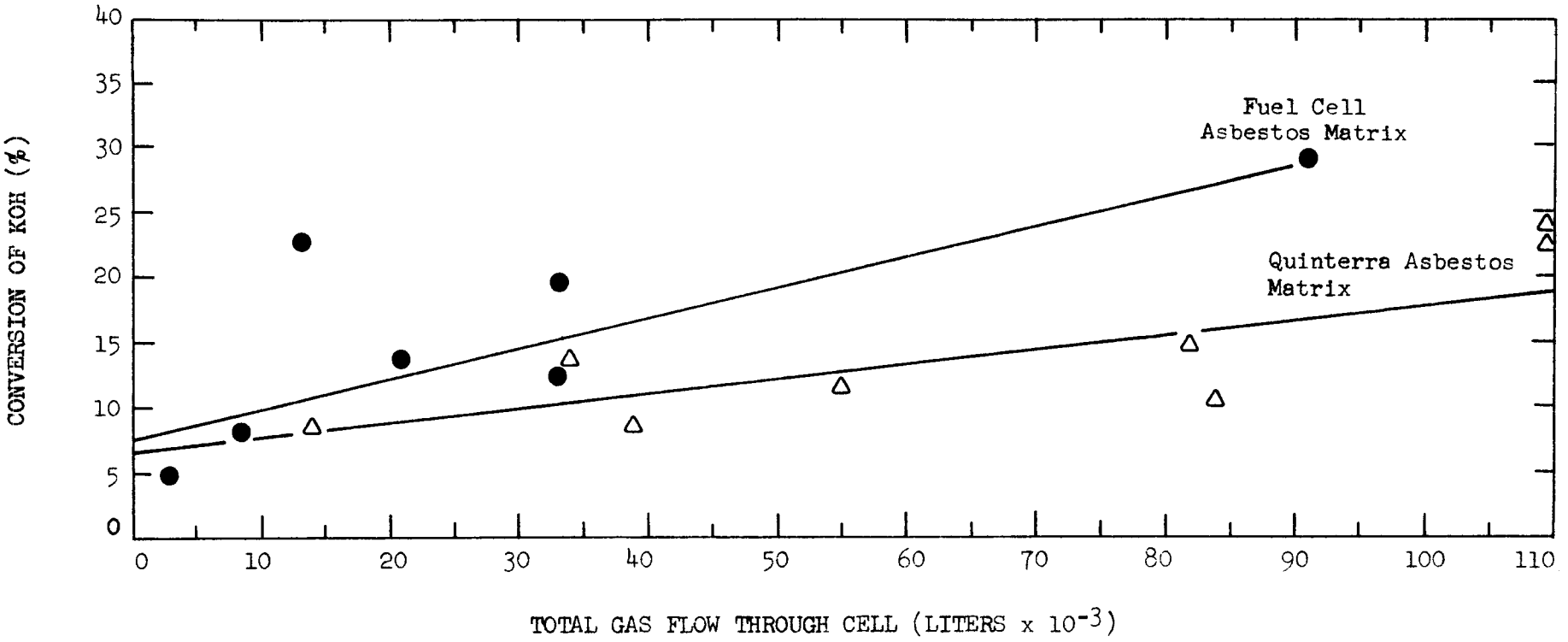


Figure 3-16

CRYSTALLITE SIZE OF LIFE-TESTED ANODES

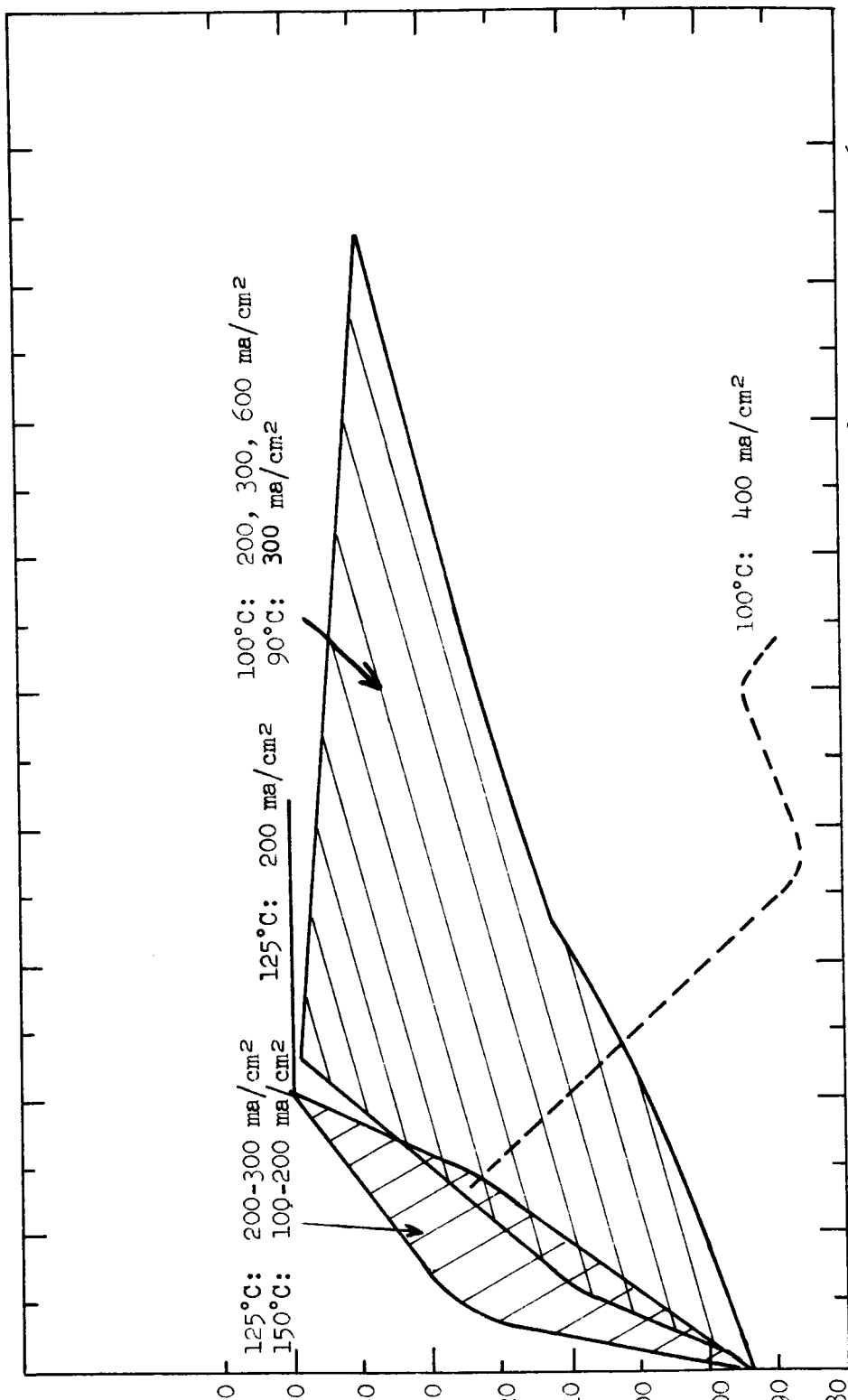


Figure 3-17

CRYSTALLITE SIZE OF LIFE-TESTED CATHODES

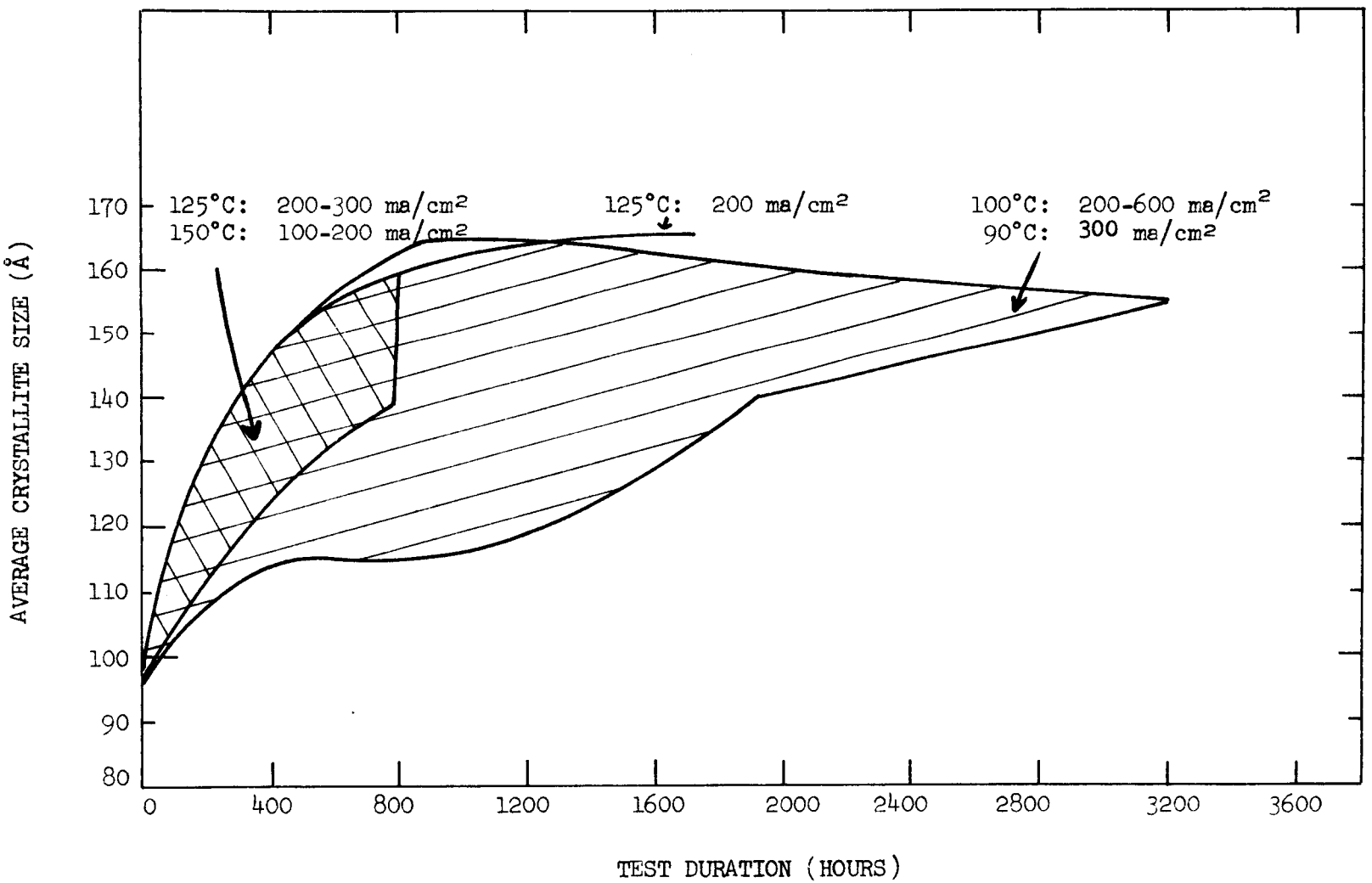


Figure 3-18

3.3.2 Pressure Life Testing

All pressure life tests were run at 45 psig with humidified gases. Cell and test station designs were described previously.[2] The two types of cells (square and round design) are shown in Figures 3-19 through 3-21. Table 3-6 summarizes test conditions and results. Most tests were run under conditions which had previously yielded stable performance at atmospheric pressure. The variations of cell voltage and resistance with time are shown in Figures 3-22 through 3-27. Tests are discussed below according to matrix type.

3.3.2.1 Tests with Fuel Cell Asbestos Matrix

Figure 3-22 shows tests with the Fuel Cell Asbestos matrix at 100°C. Test 2-492 at 100 ma/cm^2 is running at 50% KOH. The initial voltage was 0.98 v. During 568 hours, the decline rate has been nearly stable (5.0 mv/100 hours). A test at 200 ma/cm^2 (2-485) was run at 40% KOH. The initial voltage was 0.92 v and the test was unstable during 96 hours.

3.3.2.2 Tests with Quinterra Asbestos Matrix

All tests with Quinterra Asbestos as the matrix were run at 100°C and 50% KOH, at the same inlet gas dew point (55°C) and exit H_2/O_2 ratio (1.0). The matrix has relatively poor wet strength and broke within the land and groove area in 12 start-ups.

Figure 3-23 shows tests at 100 ma/cm^2. The average initial voltage was 0.99 v. Test 2-440 with a KOH loading of 3.0 g/g matrix was very stable for 350 hours at 0.98-0.99 v., giving a decline rate of only 0.5 mv/100 hours. The test was terminated when an emergency shutdown switch was accidentally tripped. Two tests (2-453 and -464) employing lower KOH loadings (2.0-2.5 g/g matrix) were unstable during periods of 160-230 hours.

Tests at 200 ma/cm^2 are shown in Figure 3-24. In four tests, the initial voltage was 0.93-0.95 v, and averaged 0.94 v. Test 2-486 operating at a KOH loading of 2.5 g/g matrix has run stably for 900 hours at 0.94 v and a decline rate of 1.6 mv/100 hours. By contrast, three tests at lower loadings (2.0 g/g matrix) were very unstable (2-443, -450 and -459).

3.3.2.3 Tests with Ceria-PTFE Matrix

All tests with the 95/5 Ceria-PTFE matrix were run at 125°C. Early tests employed 60% KOH but at the request of the NASA Project Manager, later tests were limited to a maximum concentration of 50%. 50% KOH is potentially advantageous because it is below the room temperature solubility limit (52%) and thus would permit a battery system to be shut down and then re-started at room temperature without first diluting the electrolyte. This potential advantage is gained at the expense of a decrease in performance level at current densities up to 300-400 ma/cm^2.

Figure 3-25 shows tests at 100 ma/cm^2. Two tests were run at 60% KOH (2-438 and -456). Test 2-438, continued from the previous contract was very stable for 540 hours at an impressively high voltage level (1.02 v). The decline rate was only 0.5 mv/100 hours. Similar excellent level of performance was obtained in a duplicate test (2-456) which ran at 1.02 v for 61 hours. Both tests were terminated when an emergency shutdown switch was tripped accidentally. Test 2-461 run at 50% KOH was extremely stable for 660 hours at 0.99 v with no voltage decline. The voltage continued constant at this high level for another 225 hours despite leakage of electrolyte out of the cell. Thereafter, a severe gas leak terminated the run.

Tests at 200 ma/cm^2 are shown in Figure 3-26. Test 2-439, with 60% KOH, ran stably for 860 hours at an outstanding voltage level (0.99-1.00 v). The decline rate was 1.2 mv/100 hours. The test was terminated when temporary interruption in the building power supply opened the emergency solenoid valves in the gas exit lines and released the cell pressure. A second test at 60% KOH (2-452) had a relatively low initial voltage (0.97 v) for these operating conditions and was unstable during 235 hours.

Test 2-467 employed 50% KOH. The cell operated stably for 1360 hours at 0.95-0.96 v and a decline rate of 0.7 mv/100 hours. Thereafter, the matrix broke causing a gas cross leak and terminating the test.

Thus far, 1360 hours represents the longest period of operation at 125°C for a Ceria-PTFE matrix without breakage. A second test at 50% KOH (2-462) operated erratically during 146 hours and was terminated.

A comparison of test results at 50% and 60% KOH shows the substantial performance advantage at 100-200 ma/cm^2 (30-50 mv) which is gained by operating at the higher concentration.

Two tests were started at <u>300 ma/cm^2</u> (Figure 3-27) with a relatively thin matrix (15-16 mils compared to the usual 20-30 mils). Both had very high initial voltages (0.95-0.96 v). Test 2-493 was stable for 193 hours at an average decline rate of 4 mv/100 hours. Test 2-488 was unstable during 167 hours. Both were terminated by partial plugging in the hydrogen saturator.

TABLE 3-C

SMALL CELL PRESSURE LIFE TESTS

Cell: Two Inch
Electrodes: AB-40
Pressure: 45 psig

TLT No.	Current Density (ma/cm²)	Temp. (°C)	KOH Conc. (%)	Cell Type	Matrix Thickness (Mils)	Initial KOH Loading: g/g Matrix	Initial KOH Loading: Total[a] In Cell(g)	Inlet Gas Dew Point (°C)	Inlet Gas Flow Rate cc/min At 23° & 0 psig: H₂	Inlet Gas Flow Rate cc/min At 23° & 0 psig: O₂	Exit H₂/O₂ Ratio	Test[b] Duration (Hours)	Working Voltage(v): Initial[c]	Working Voltage(v): Final[b]	Average[b] Voltage Decline Rate (mv/100 hours)	Status	Reason For Termination
TESTS WITH FUEL CELL ASBESTOS MATRIX																	
2-492	100	100	50	Round	20	1.5	8.2	45	308	298	1.0	968	.978	.950	5.0	Continuing	—
2-485	200	100	40	Square	20	1.3	6.6	72	1150	1130	1.0	96	.924	.882	20	Terminated	(1)
TESTS WITH QUINTERRA ASBESTOS MATRIX																	
2-440	100	100	50	Square	20	3.1	9.4	55	500	490	1.0	350	.990	.979	0.5	Terminated	(2)
2-453	100	100	50	Square	20	2.0	6.6	55	500	490	1.0	160	.991	.970	10	Terminated	(2)
2-464	100	100	50	Square	20	2.5	7.9	55	500	490	1.0	232	1.006	.906	14	Terminated	(3)
2-486	200	100	50	Square	20	2.5	7.9	55	1150	1130	1.0	907	.954	.934	1.6	Continuing	—
2-443	200	100	50	Square	20	2.0	6.5	55	1000	980	1.0	237	.934	.860	32	Terminated	(4)
2-450	200	100	50	Square	20	2.0	7.0	55	1000	980	1.0	229	.943	.924	12	Terminated	(5)
2-459	200	100	50	Square	20	2.0	7.6	55	1000	980	1.0	240	.950	.917	14	Terminated	(6)
TESTS WITH CERIA-PTFE MATRIX																	
2-438	100	125	60	Round	21	~ 0.8[d]	~ 9.1[d]	55	500	490	1.0	540	1.025	1.017	0.5	Terminated	(2)
2-456	100	125	60	Round	—	—	—	55	500	490	1.0	66	1.025	1.022	—	Terminated	(2)
2-461	100	125	50	Round	—	—	—	55	114	104	1.0	0-660[e]	1.000	.990[e]	0[e]		
												660-885	.990	.994	0	Terminated	(7)
2-439	200	125	60	Round	27	~ 0.6	~ 8.0	55	1000	980	1.0	860	1.004	.989	1.2	Terminated	(4)
2-452	200	125	60	Round	—	—	—	55	1000	980	1.0	235	.966	.950	6	Terminated	(8)(9)
2-462	200	125	50	Round	—	—	—	55	228	208	1.0	146	.980	.910	(f)	Terminated	(10)
2-467	200	125	50	Round	—	—	—	55	228	208	1.0	1360	.979	.950	0.7	Terminated	(11)(8)(9)
2-493	300	125	50	Round	16	~ 1.8	~11.7	72	810	80	2.5	192	.964	.951	4	Terminated	(3)
2-488	300	125	50	Round	15	~ 1.8	~11.0	72	810	80	2.5	167	.951	.924	13	Terminated	(3)

Letter Key

(a) Of the total electrolyte in the cell, 35-40% was generally introduced in the electrolyte prior to cell assembly.
(b) Prior to any accelerated or abrupt voltage decline.
(c) Maximum voltage within first 100 hours.
(d) Ceria-PTFE matrices are kept equilibrated with water and then electrolyte before test-Accordingly loadings shown are approximate and are calculated from average value of 1.5 g dry matrix/cc water-wet matrix.
(e) Prior to leakage of KOH out of cell.
(f) Voltage erratic

Reasons for Termination

(1) Low pressure cut-off switch tripped while adjusting flow.
(2) Emergency shutdown switch tripped accidentally.
(3) Plug in saturator.
(4) Building power failure.
(5) High temperature cut-off switch tripped when jarred.
(6) Loss of hydrogen pressure.
(7) Leaking cell.
(8) Gas cross-leak.
(9) Accelerated voltage decline.
(10) Voltage erratic
(11) Matrix broke.

TWO INCH PRESSURE CELL: SQUARE DESIGN

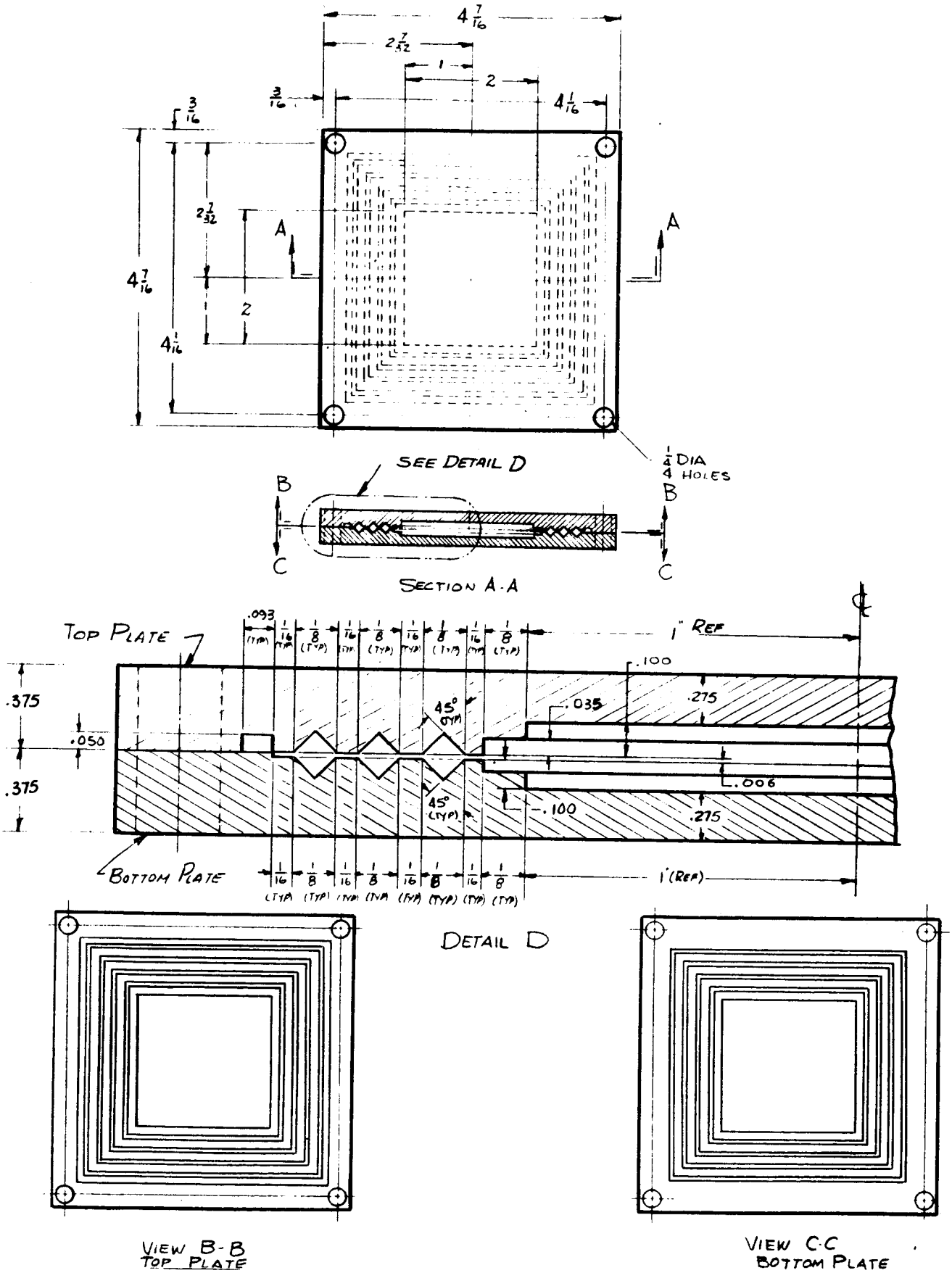


Figure 3-19

TWO INCH PRESSURE CELL: ROUND DESIGN

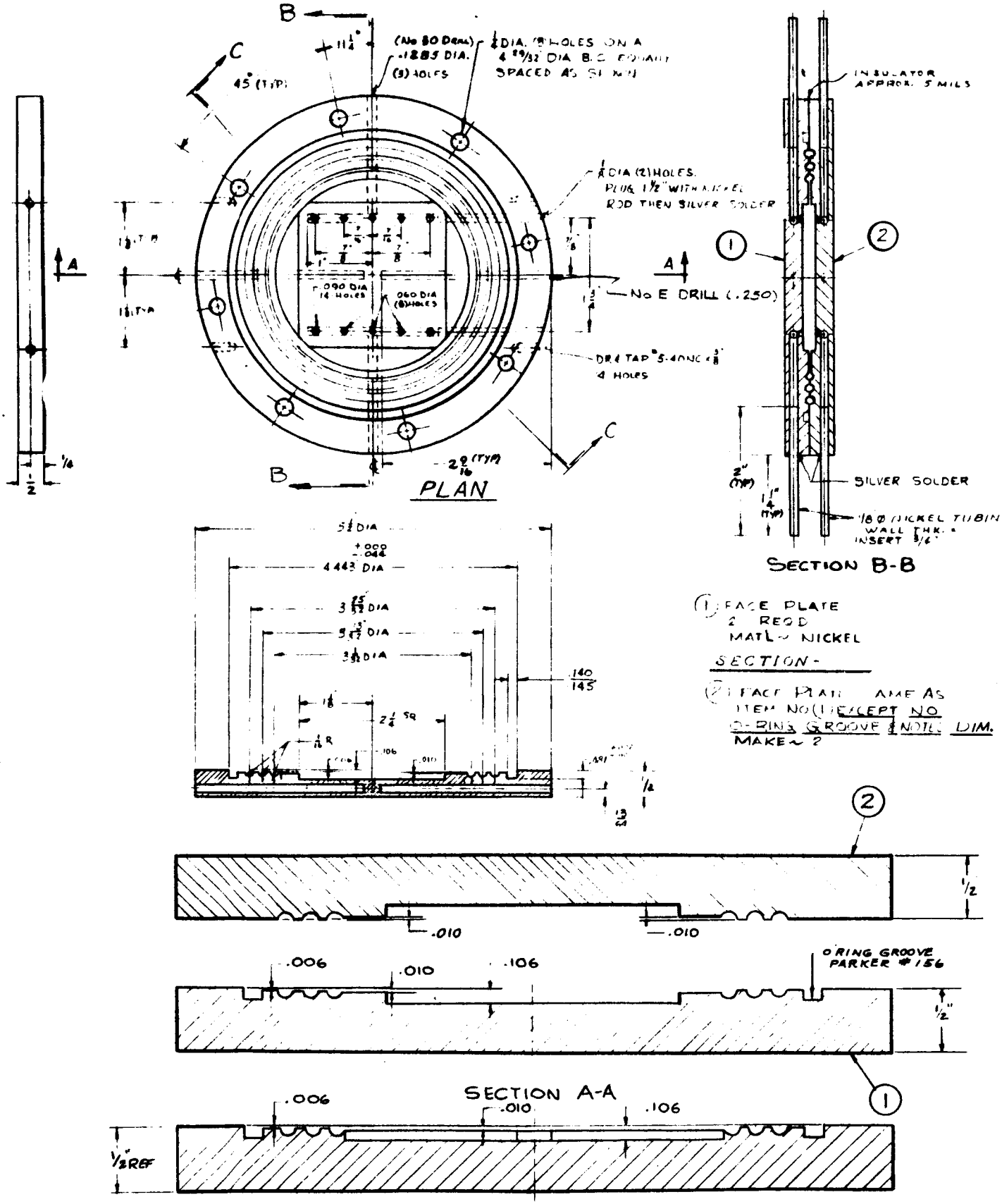


Figure 3-20

TWO INCH PRESSURE CELL: ROUND DESIGN

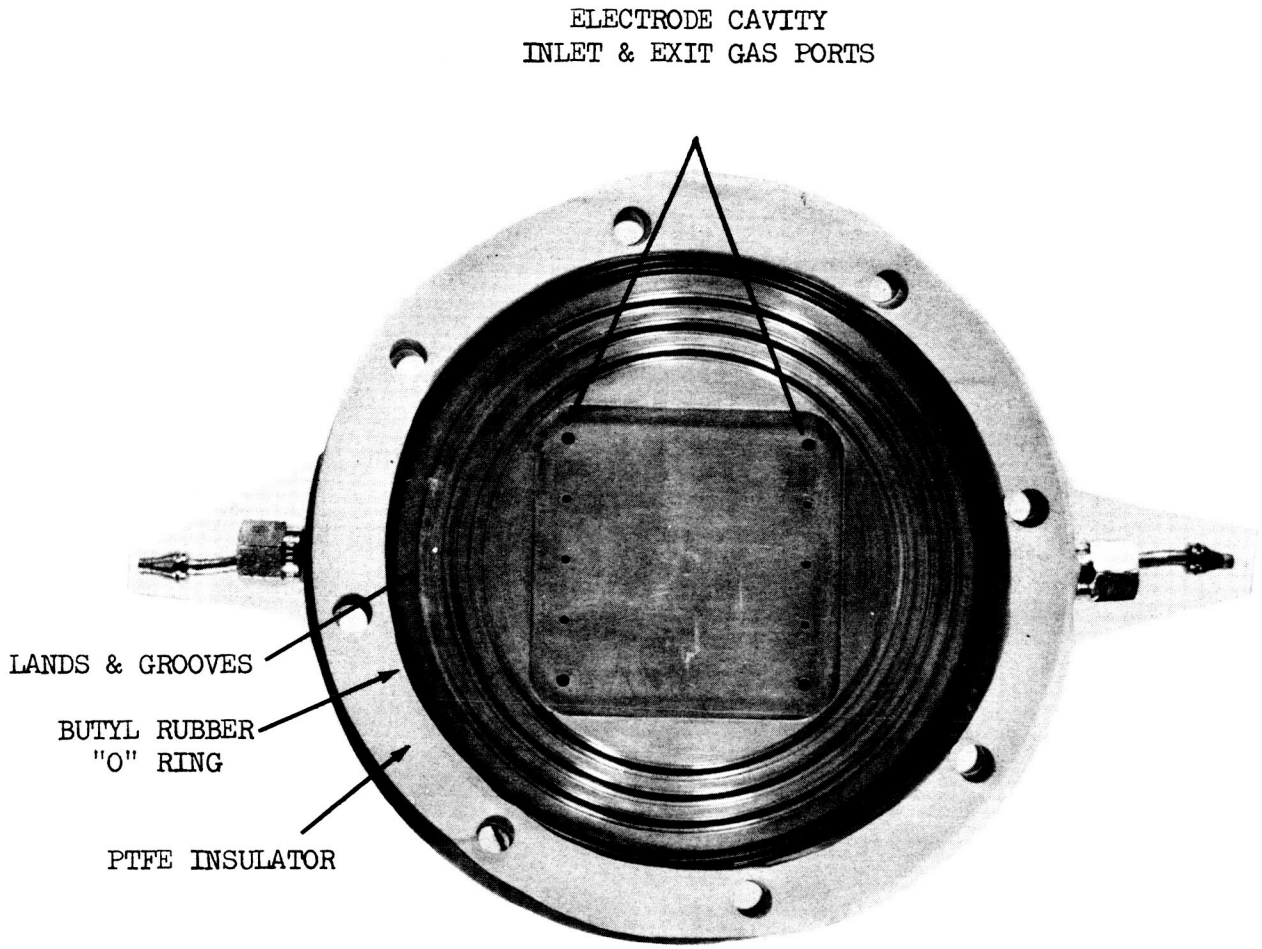


Figure 3-21

SMALL CELL PRESSURE LIFE TESTS
FUEL CELL ASBESTOS MATRIX: 100°C: 100-200 ma/cm²
Pressure: 45 psig
100 ma/cm²: 50% KOH: 2-492
200 ma/cm²: 40% KOH: 2-485

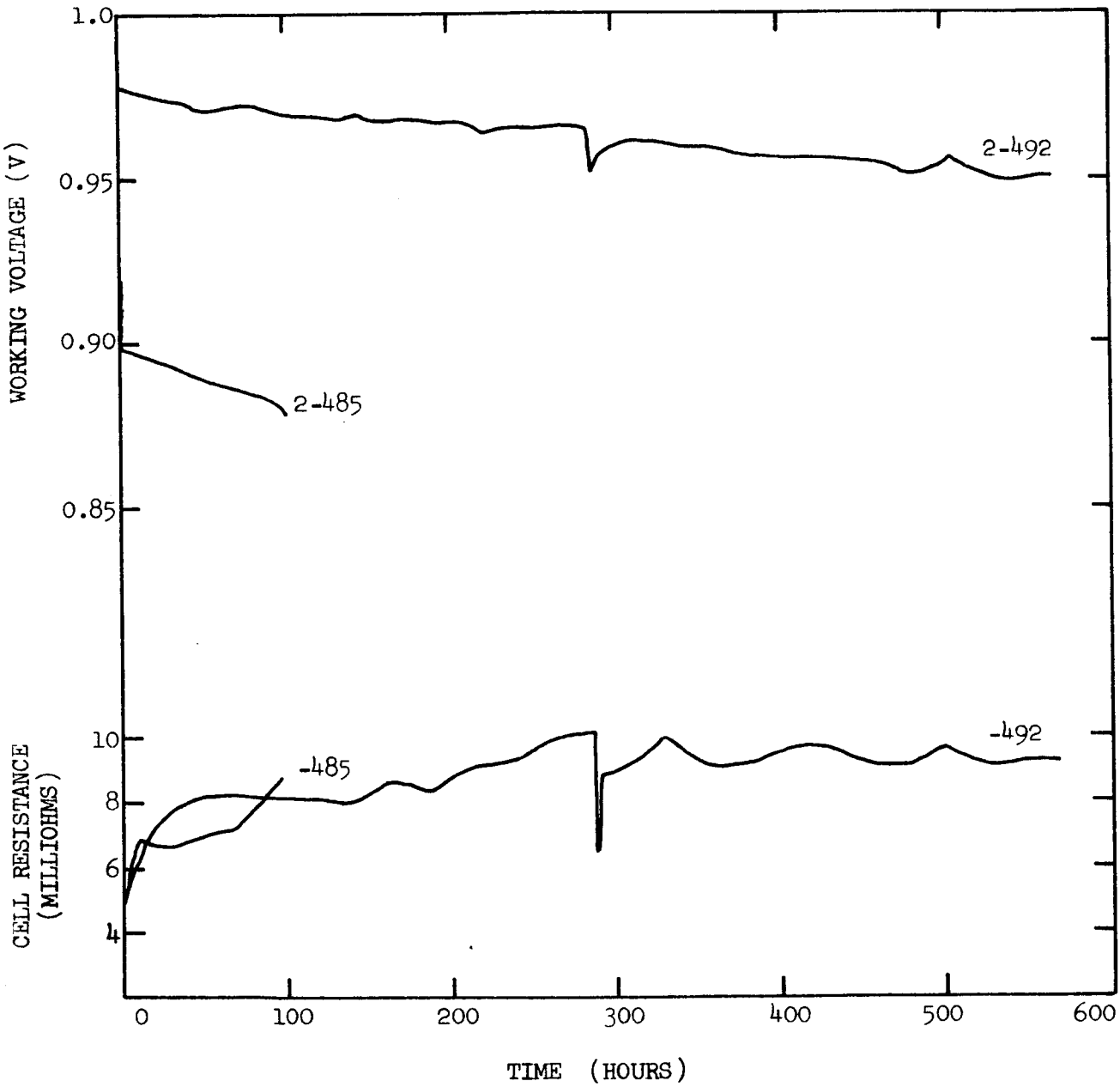


Figure 3-22

SMALL CELL PRESSURE LIFE TESTS
QUINTERRA ASBESTOS MATRIX: 100°C: 100 ma/cm²

Pressure: 45 psig
KOH Conc.: 50%

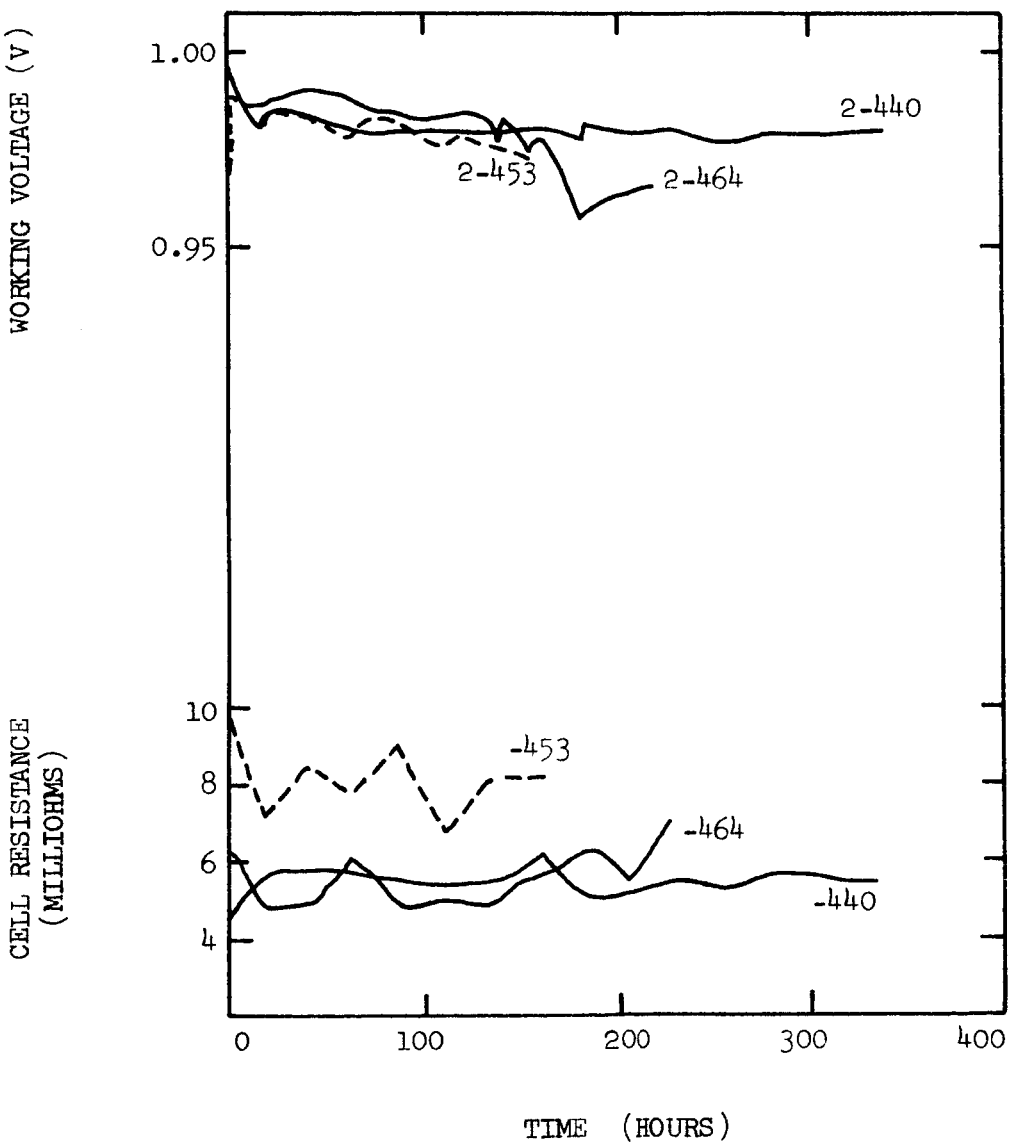


Figure 3-23

SMALL CELL PRESSURE LIFE TESTS
QUINTERRA ASBESTOS MATRIX: 100°C: 200 ma/cm²

Pressure: 45 psig
KOH Conc.: 50%

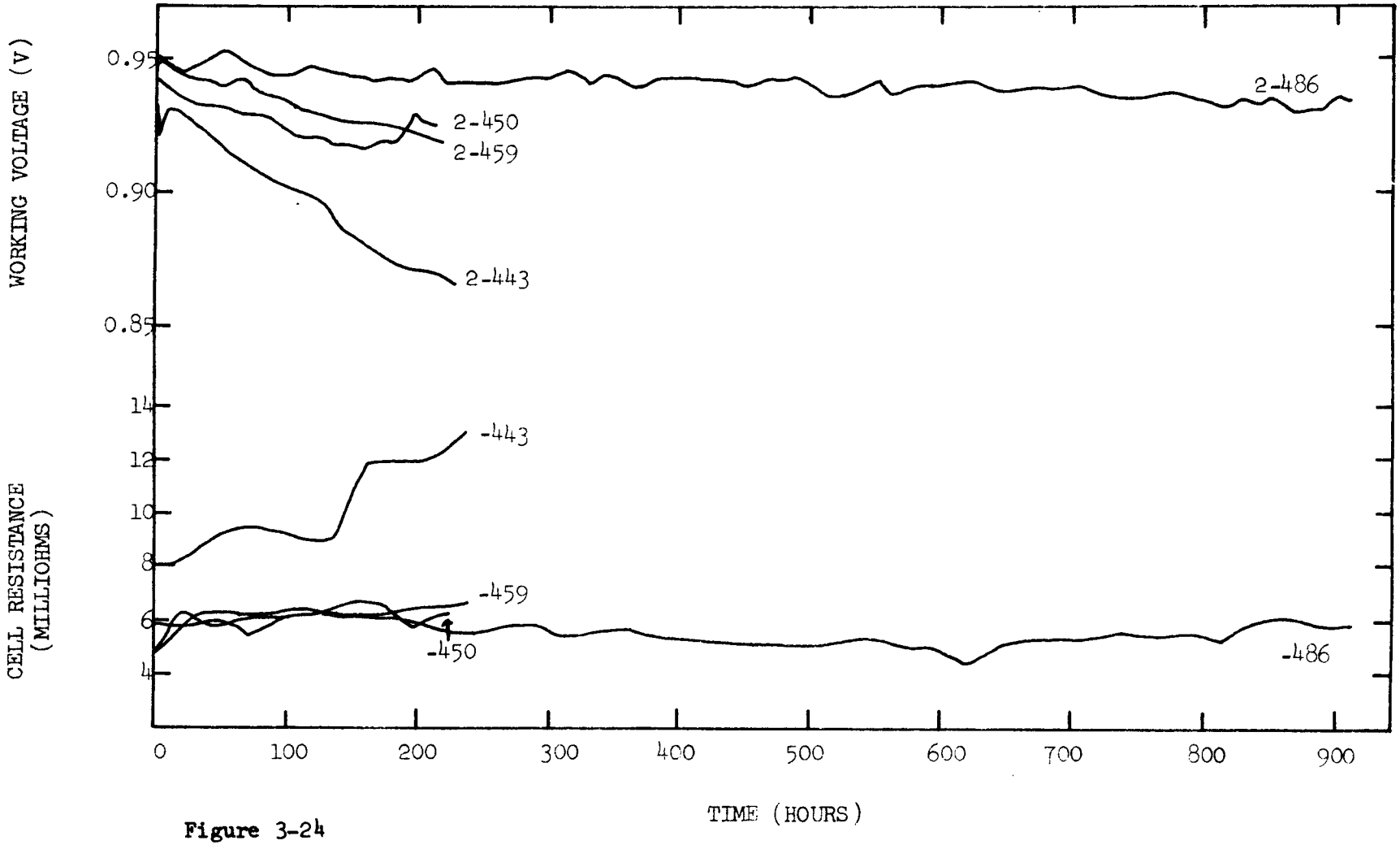


Figure 3-24

SMALL CELL PRESSURE LIFE TESTS
CERIA-PTFE MATRIX: 125°C: 100 ma/cm²

Pressure: 45 psig
50% KOH: 2-461
60% KOH: 2-438

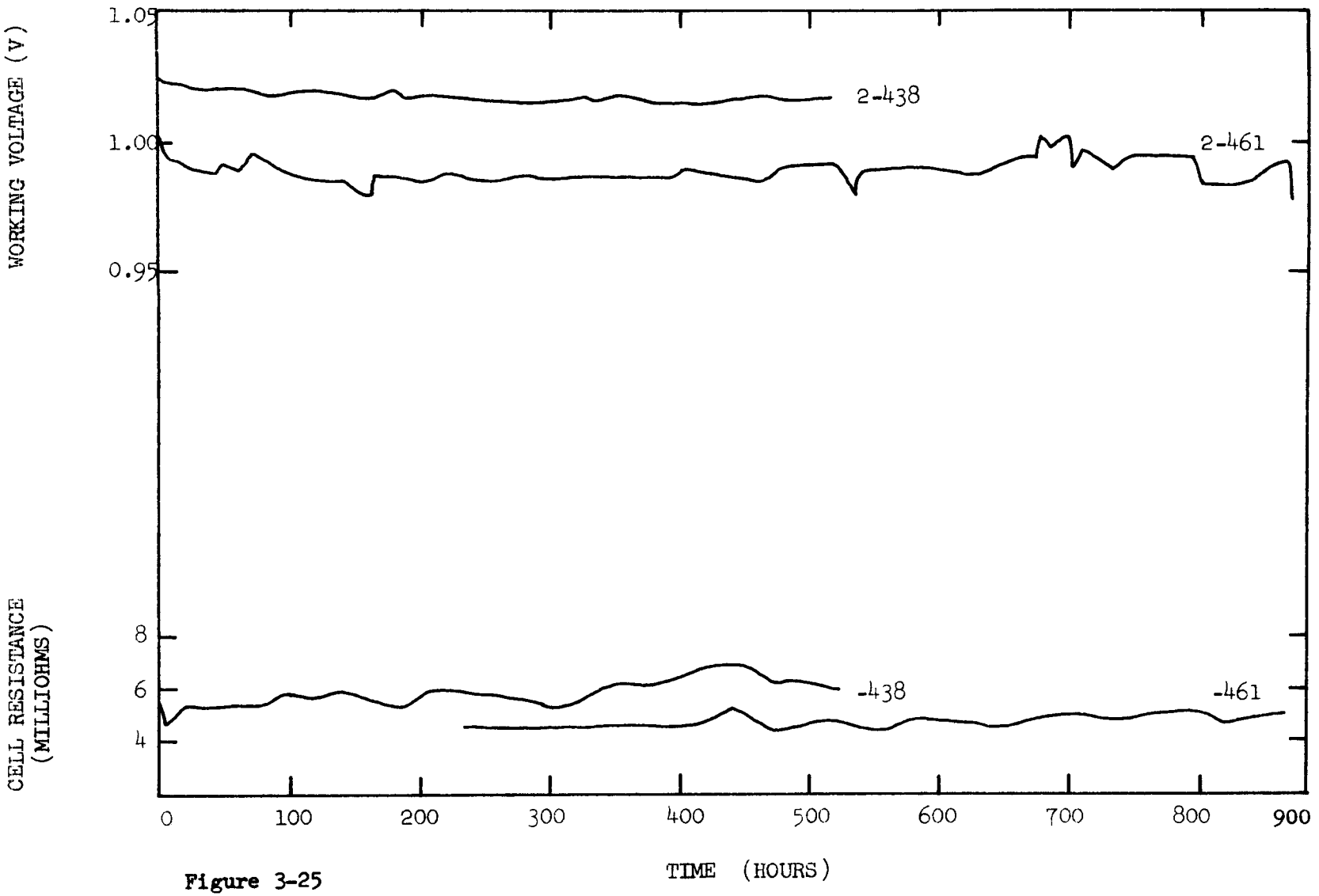


Figure 3-25

SMALL CELL PRESSURE LIFE TESTS
CERIA-PTFE MATRIX: 125°C: 200 ma/cm^2

Pressure: 45 psig
50% KOH: 2-462, 2-467
60% KOH: 2-439, 2-452

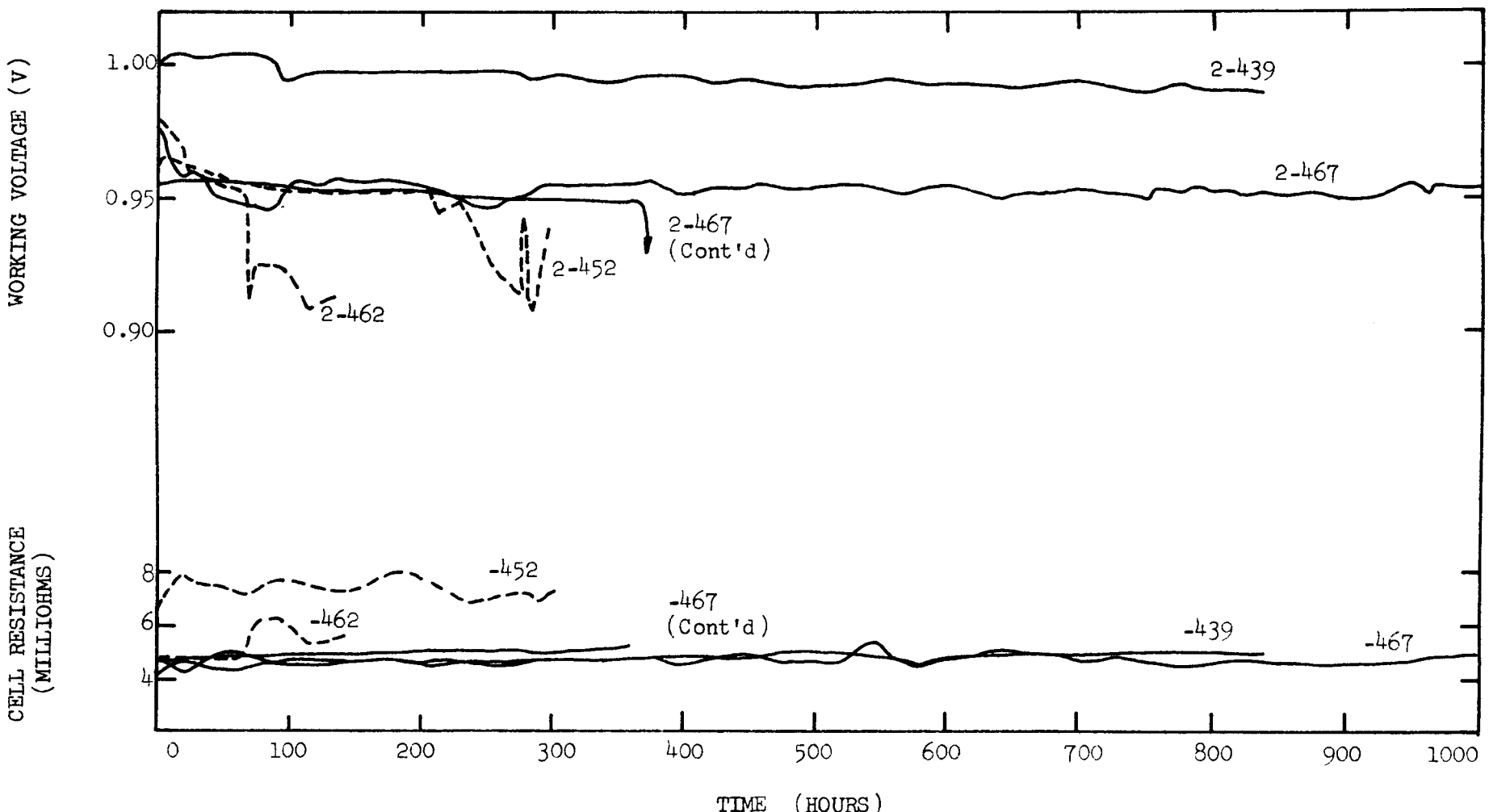


Figure 3-26

SMALL CELL PRESSURE LIFE TESTS
CERIA-PTFE MATRIX: 125°C: 300 ma/cm²

Pressure: 45 psig
KOH Conc.: 50%

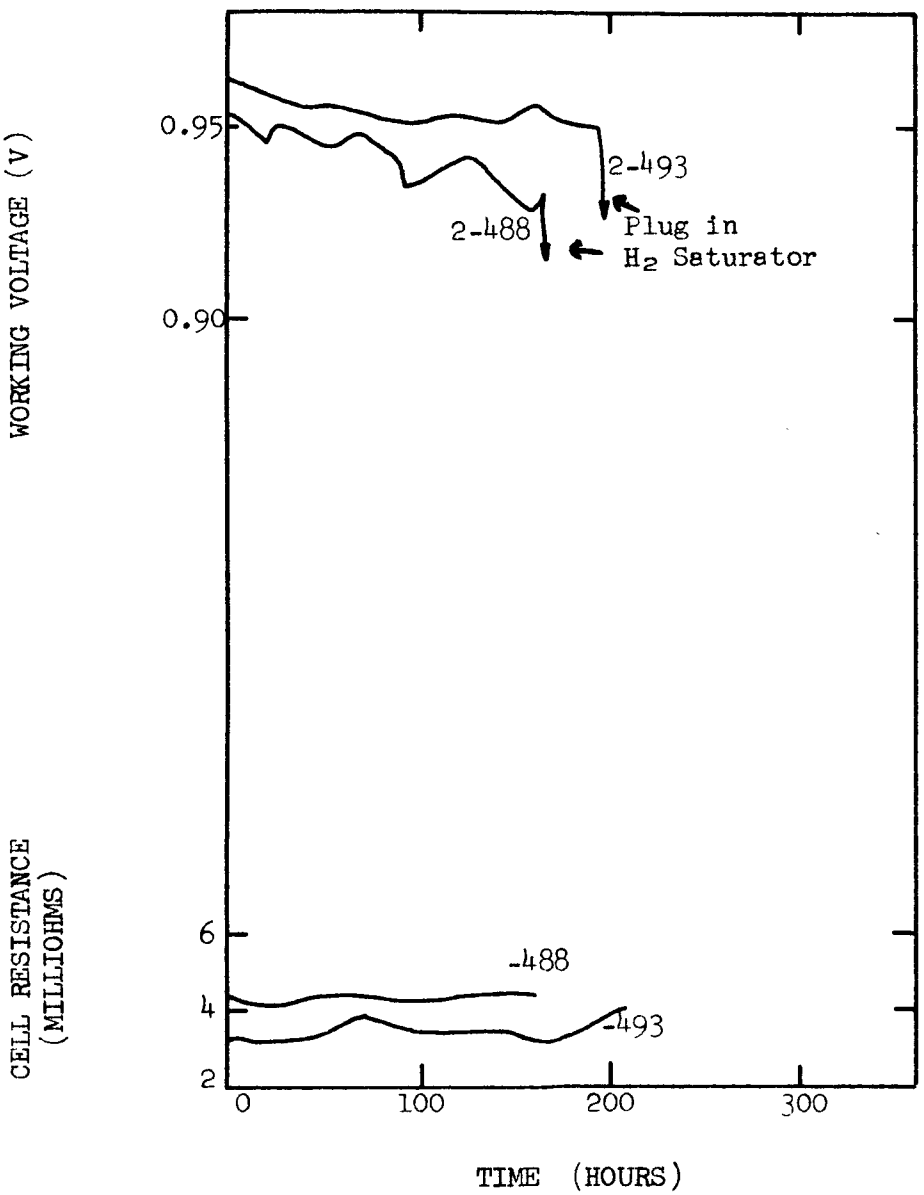


Figure 3-27

4. LARGE CELL TESTING

Large cell testing aimed at duplicating with battery-size electrodes the stable performance attained in samll cell life tests. Quinterra Asbestos, Fuel Cell Asbestos and Ceria-PTFE were employed as matrices in this effort. Major emphasis was place on operating with Quinterra Asbestos because of its demonstrated superiority over the other two at very high current densities (300-600 ma/cm^2).

4.1 Test Stations

At the start of this contract, two test stations were available: one for operation with dry gases only and the other for operation with dry gases or with gases humidified in small vaporizers. These stations have been described in detail.[2]

During the current period, a new five station facility was designed and contructed. The stations are suitable for operation with either dry or humidified gases at pressures up to at least 60 psig. An overall view of the stations is given in Figure 4-1 while Figure 4-2 shows one of the stations in more detail.

A schematic view of a typical station is shown in Figure 4-3. Hydrogen (General Dynamics) is supplied from a tank truck and contains less than one ppm carbon dioxide. Oxygen (General Dynamics) is vaporized from a liquid supply tank and contains less than one ppm carbon dioxide. In order to further insure a negligible carbon dioxide content, both gases are passed through Ascarite scrubbers located in the main line.

At a station each gas flows through a solenoid valve, pressure regulator and flowmeter and is then humidified in a small vaporizer before entering the cell. Gas flow rates are controlled by needle valves positioned downstream from the cell. Water is fed to each vaporizer from a supply tank pressurized with nitrogen to 15 psig above that of the reactant gases. Needle valves control the water feed rate.

The vaporizer is shown schematically in Figure 4-4. Its temperature is 150-170°C and, like that of the cell, is maintained by an on-off controller. Water enters the top section of the vaporizer which is packed with stainless steel turnings and is vaporized into the gas stream entering at the bottom. The asbestos which insures a steady rather than a dropwise flow of water into the vaporizer and the packing which provides greater heated surface area, prevent too rapid flashing which leads to undesirable pressure surges. Lines from the vaporizers to the cell and from the cell to the flow control valves are heated to prevent condensation.

The stations have several safety devices designed to prevent the formation of an explosive mixture of hydrogen and oxygen in the system in case of cross-leakage through the cell matrix. Single and double check valves are used to prevent any back flow of gas to the vaporizer or the water feed tank. In the event of emergency, provision is made for rapidly releasing the reactant gases through a solenoid valve in a branch of each line leaving the cell. Simultaneously, solenoid valves located upstream from the cell shut off the gas and water feeds to the station, open nitrogen purges to both sides of the system and shut off the cell heater.

The entire sequence can be initiated through a manual switch. It can also be triggered automatically by a 5 psig rise or fall in system pressure (through Mercoid pressure switches), by a 10°C rise in cell temperature (through a high temperature cut-off instrument) or by a failure in the vaporizer heater (through a low temperature cut-off instrument). The drop in system pressure following shutdown trips the low pressure switch which prevents the system from re-starting on its own. Manual switches which by-pass these pressure and temperature safety devices permit test start-up.

4.2 Test Cells

Five "six inch" cells, fabricated during the previous NASA Contract,[2] were used for life testing. The cells house six inch square electrodes (234 cm^2 active area) and can withstand gas pressure up to at least 60 psig. Figure 4-5 shows their initial design which was described previously.[2] Although Fuel Cell Asbestos could be assembled in these cells satisfactorily, difficulties were encountered in assembling them with Quinterra Asbestos whose poor wet strength caused it to break repeatedly and cause gas cross-leaks prior to start-up. Breakage occurred principally in the area between the electrode cavity and the concentric ring seal area and in most cases probably resulted from hydraulic rupture of the matrix. To minimize this problem, closely spaced linear grooves were machined in the segment areas of four face plates as shown in Figure 4-6. The purpose of these grooves is to provide a reservoir for any electrolyte squeezed out of the matrix during compression. In addition, the minimum gaps available for the matrix were decreased. Thus as originally

fabricated, the active area and segment areas of each face plate was undercut 5 mils below the seal area which in turn was undercut 5 mils below the area outside of the "O" ring. This limited the minimum gap for the matrix to 12 mils in the circular groove seal area and to 22 mils in the active area and segment areas when the cell was assembled with the thinnest available insulator (2 mil) outside of the "O" ring. The latter undercuts were eliminated in both face plates of two cells in order to reduce these minimum gaps to 2 mils and 12 mils respectively. This modification permitted greater degrees of matrix compression to be applied.

4.3 Test Results

Figure 4-7 shows the different cell configurations, varying with respect to groove locations and undercut dimensions, which were employed in test start-ups. Table 4-1 summarizes cell configurations, cell assembly conditions and gas cross-leakage data for these start-ups. In some assemblies, all grooves were packed with dry asbestos in order to physically support the matrix while still maintaining an excess electrolyte reservoir. The electrodes and spacer screens were cut to fit snugly into the electrode cavity and prevent possible drooping of matrix within the cavity. The two face plates were insulated from each other outside the "O" ring seal by either 5-10 mil PTFE or by 2 mil fluorocarbon polymer film. Life test conditions and results for those assemblies which were free of cross-leaks are given in Table 4-2.

4.3.1 Tests With Quinterra Asbestos Matrix

Twenty-six assemblies were made with 20 mil Quinterra Asbestos matrices in five different cell configurations. Gaps provided for the matrix ranged from 5-23 mils in the seal area to 15-32 mils in the active area and segment areas. Since the dry matrix swells to approximately 50 mils when wet with electrolyte, it was compressed approximately 54-90% and 36-70% in these respective areas.

During all start-ups the cells developed a cross-leak evidenced in most cases by imposing a 2 psig differential pressure across the matrix, either of nitrogen at room temperature or of hydrogen at 100°C. In most cases, cross-leaks were caused by tears or pinholes, which developed after the assembly, in the seal area, in the segment area, or along the electrode edges. In a few assemblies, cross-leaks occurred even in the absence of any visible openings in the matrix.

Cell configuration (2) caused less matrix tearing and less cross-leakage than configuration (1), at nearly identical matrix compression, when the grooves were not packed with asbestos. With both configurations, packing the grooves lessened matrix tearing but did not lessen cross-leakage.

No consistent effect of matrix compression on the amount of tearing is evident, partly because the results were not reproducible. Thus, when these gaps in the seal area and active area were 19 mils and 25 mils respectively (Configuration 2), nitrogen did not cross-leak in two assemblies (holding in one case a 10 psig pressure differential for nearly two hours) but did cross-leak in three other apparently identical

assemblies. Nitrogen cross-leaks were also prevented in one assembly with a 5 mil gap in the active area and a 15 mil gap in the seal area (Configuration 4). The results were not reproducible partly because the seals that were established were "borderline". Thus two of the assemblies which did not cross-leak with nitrogen cross-leaked with hydrogen under the same differential pressure, either at room temperature or at 100°C.

Better sealing was obtained with 30 mil thick matrices in cell configurations (1) and (2). Thus, in all five assemblies with a 18-19 mil gap in the seal area and a 25-27 mil gap in the active area, no cross-leaks were encountered with a 2-10 psig differential of nitrogen at room temperature. Three of these assemblies also did not cross-leak with a 2 psig differential of hydrogen at 100°C. However, cell polarizations obtained for these assemblies showed poor initial performance, particularly at current densities above 100 ma/cm^2, compared to that of a 20 mil matrix in a two inch cell (Figure 4-8). Additional work is required to determine the cause.

One life test was started with the 30 mil matrix at 100°C, 45 psig, 50% KOH and 100 ma/cm^2 on dry gases (7344-179). The voltage declined rapidly from 0.902 v to 0.877 v during 21 hours without any significant rise in cell resistance. The voltage was increased to 0.896 v during the next 27 hours by lowering the gas flows to maintain a 40% KOH concentration in the cell. The test was terminated by a loss of hydrogen line pressure.

Preliminary studies with the 20 mil Quinterra Asbestos matrix in a flat plate six inch cell were carried out using silicone rubber gaskets taped with PTFE to form the active area and maintain the seal. This cell, whose design has been described in detail,[1] had previously operated satisfactorily at atmospheric pressure with ACCO-I Asbestos as the matrix.[2] Improved techniques for taping the gaskets were developed to enable the cell to hold 45 psig without leaking, both at ambient temperature and at 100°C. The Quinterra matrix broke severely within this cell when no frame was used to limit its compression. A 10 mil PTFE frame prevented breakage at room temperature but not at 100°C. Additional work is planned at lower compression.

4.3.2 Tests with Fuel Cell Asbestos Matrix

After several unsuccessful attempts, both 15 and 20 mil Fuel Cell Asbestos matrices were assembled in cell configurations (3) and (1) without breakage or gas cross-leakage. Figure 4-9 shows polarization curves obtained with these matrices at 100°C, 45 psig and 50% KOH. The performance of the 20 mil matrix was the same as that in two inch cells at current densities up to 200 ma/cm^2, but was lower at higher current densities. The performance of the 15 mil matrix was normal at current densities up to approximately 400 ma/cm^2, but was again lower at higher current densities.

The assembly with the 15 mil matrix was put on life test at 100 ma/cm^2 on dry inlet gases (8136-54). During 116 hours, the voltage declined 52 mv and the test was terminated (Figure 4-10).

4.3.3 Test with Ceria-PTFE Matrix

No breakage of the matrix or gas cross-leakage occurred during start-up of a cell (Configuration 3) which was assembled with the 95/5 Ceria-PTFE matrix. A life test (8136-96) was run at 125°C, 45 psig, 50% KOH, and 100 ma/cm^2 on dry gases. The initial voltage was low (0.93-0.86 v) and performance was erratic during 210 hours of operation (Figure 4-10)

TABLE 4-1

ASSEMBLY CONDITIONS FOR SIX INCH PRESSURE CELLS

Test Start-Up	Cell Configuration No.	Dry[a] Matrix Thickness (Mils)	PTFE[b] Insulator Thickness (Mils)	Gap for Matrix (Mils) in: Circular Groove Seal Area	Gap for Matrix (Mils) in: Active Area & Segment Area	Grooves Packed With Asbestos	No Cross-Leakage With:	Cross-Leakage With:	Location of Tears or Pinholes In Matrix
Quinterra Asbestos Matrix									
7676-165-3	(1)	20	0[c]	13	22	No	--	N_2 at 23°C	(i) (j)
7676-167-1	(1)	20	0[c]	13	22	Yes	--	N_2 at 23°C	(k)
7676-146	(1)	20	5	18	27	No	--	N_2 at 23°C	(i) (j)
7676-152	(1)	20	5	18	27	No	--	N_2 at 23°C	(i) (j)
7676-163-2	(1)	20	5	18	27	No	--	N_2 at 23°C	(i) (j)
7344-134	(1)	20	5	18	27	No	--	N_2 at 23°C	(j)
7676-167-2	(1)	20	5	18	27	Yes	--	N_2 at 23°C	(i) (j)
7676-167-3	(1)	20	5	18	27	Yes	--	N_2 at 23°C	(j)
7676-167-4	(1)	20	5	18	27	Yes	--	N_2 at 23°C	None
7676-169-1	(1)	20	5	18	27	Yes	--	N_2 at 23°C	None
7676-154	(1)	20	10	23	32	No	--	N_2 at 23°C	(i) (j)
7676-169-2	(2)	20	2[d]	16	22	Yes	--	N_2 at 23°C	(k)
7344-190	(2)	20	2[d]	16	22	Yes	N_2 at 23°C	N_2 at 23°C	--
7676-161	(2)	20	5	19	25	No	--	N_2 at 23°C	(i)
7676-162	(2)	20	5	19	25	No	N_2 at 23°C	--	(i)
7676-163-1	(2)	20	5	19	25	No	N_2 at 23°C[e]	--	(k)
7676-165-1	(2)	20	5	19	25	No	--	N_2 at 23°C	(k)
7676-165-2	(2)	20	5	19	25	No	--	N_2 at 23°C	(i)
7676-166-1	(2)	20	5	19	25	No	--	N_2 at 23°C	(j) (k)
7676-166-3	(2)	20	5	19	25	Yes	--	N_2 at 23°C	None
7676-166-4	(2)	20	5	19	25	Yes	--	N_2 at 23°C	None
7676-172	(2)	20	5	19	25	Yes	--	N_2 at 23°C	(k)
8136-34	(3)	20	10	10	20	--	--	N_2 at 23°C	(k)
8136-45	(3)	20	10	10	20	Yes	--	N_2 at 23°C	(k)
8136-32	(4)	20	5	5	15	--	N_2 at 23°C	H_2 at 100°C	None
7676-166-2	(5)	20	5	16	23	No	--	N_2 at 23°C	(j)
8136-61[f]	Flat Plate type	20	--	--	--	--	--	N_2 at 23°C	(l)
8136-62[g]	Flat Plate type	20	--	--	--	--	N_2 at 23°C	H_2 at 100°C	(l)
7344-156	(1)	30	5	18	27	No	N_2 at 23°C	H_2 at 100°C	--
7676-169-3	(2)	30	5	19	25	Yes	N_2 at 23°C H_2 at 100°C	--	--
7676-174	(2)	30	5	19	25	Yes	N_2 at 23°C H_2 at 100°C	--	None
7344-178	(2)	30	5	19	25	Yes	N_2 at 23°C	H_2 at 100°C	--
7344-179	(2)	30	5	19	25	Yes	N_2 at 23°C H_2 at 100°C	--	--
Fuel Cell Asbestos Matrix									
8136-48-3	(3)	15	10	10	20	No	--	N_2 at 23°C	(j)
8136-48-4	(3)	15	10	10	20	Yes	--	N_2 at 23°C	(j)
8136-49-1	(3)	15	10	10	20	Yes	--	N_2 at 23°C	None
8136-49-2	(3)	15	10	10	20	Yes	--	N_2 at 23°C	(k)
8136-53	(3)	15	10	10	20	Yes	N_2 at 23°C H_2 at 100°C	--	
7676-158-2	(1)	20	5	18	27	No	--	N_2 at 23°C	(i)
7676-164	(1)	20	5	18	27	No	N_2 at 23°C H_2 at 100°C	--	None
7676-158-1	(1)	20	10	23	32	No	--	N_2 at 23°C	None
7676-160	(2)	20	5	19	25	No	--	N_2 at 23°C	None
Ceria-PTFE Matrix									
8136-96	(3)	15-23[h]	5	5	15	No	H_2 at 125°C	--	--

NOTES

(a) When wet with electrolyte uncompressed 20 mil Fuel Cell Asbestos and Quinterra Asbestos swell to 28-30 mil and approximately 50 mils thick respectively.

(b) Insulator is of PTFE, unless specified otherwise.

(c) Insulator omitted to determine effect of mimimum matrix gap spacing with this cell configuration on matrix breakage.

(d) Fluorocarbon film insulator.

(e) No cross-leakage under a 10 psig differential pressure for 110 mins.

(f) No frame around matrix to limit compression.

(g) PTFE frame around matrix limited compression to 10 mils.

(h) Thickness of matrix saturated with electrolyte.

(i) Tears or pinholes in matrix adjacent to circular groove area of face plates.

(j) Tears of pinholes in matrix adjacent to segment areas of face plates.

(k) Tears or pinholes in matrix near edge(s) of electrodes.

(l) Tears or pinholes in matrix between electrodes and gaskets of flat plate cell.

TABLE 4-2

LARGE CELL PRESSURE LIFE TESTS

Cell: Six inch
Pressure: 45 psig
Inlet Gases: Dry

TLT No.	Matrix	Thickness (Mils)	Current Density (ma/cm^2)	Temp. (°C)	Nominal KOH Conc. (%)	Initial KOH Loading g/g Matrix	Initial KOH Loading Total[a] In Cell (g)	Inlet Gas Flow Rate (cc/min. at 23°C and 0 psig) H_2	Inlet Gas Flow Rate (cc/min. at 23°C and 0 psig) O_2	Exit H_2/O_2 Ratio	Test Duration (Hours)	Working Voltage (v) Initial	Working Voltage (v) Final[b]	Average[c] Voltage Decline Rate (mv/100 hours)	Status	Reason For Termination
7344-179	Quinterra Asbestos	30	100	100	50	2.0	63	1365	1275	1.0	0-21	.902	.877			
					40			520	725	0.7	21-48	.877	.896		Terminated	(1)
8136-54	Fuel Cell Asbestos	15	100	100	50	1.5	42	1185	1185	1.0	116	.980	.928	45	Terminated	(2)
8136-96	Ceria-PTFE	19	100	125	50	1.5	85	617	577	1.0	210	.922	.892	(d)	Terminated	(3)

GENERAL NOTES

(a) 30-45% of the total electrolyte in the cell was introduced in the electrolyte prior to cell assembly.

(b) Final voltage prior to test failure.

(c) Average slope of voltage-time plot.

(d) Voltage erratic.

REASONS FOR TERMINATION

(1) Loss of line H_2 pressure

(2) High voltage decline rate.

(3) Loss of O_2 pressure.

LARGE CELL PRESSURE LIFE TEST STATIONS

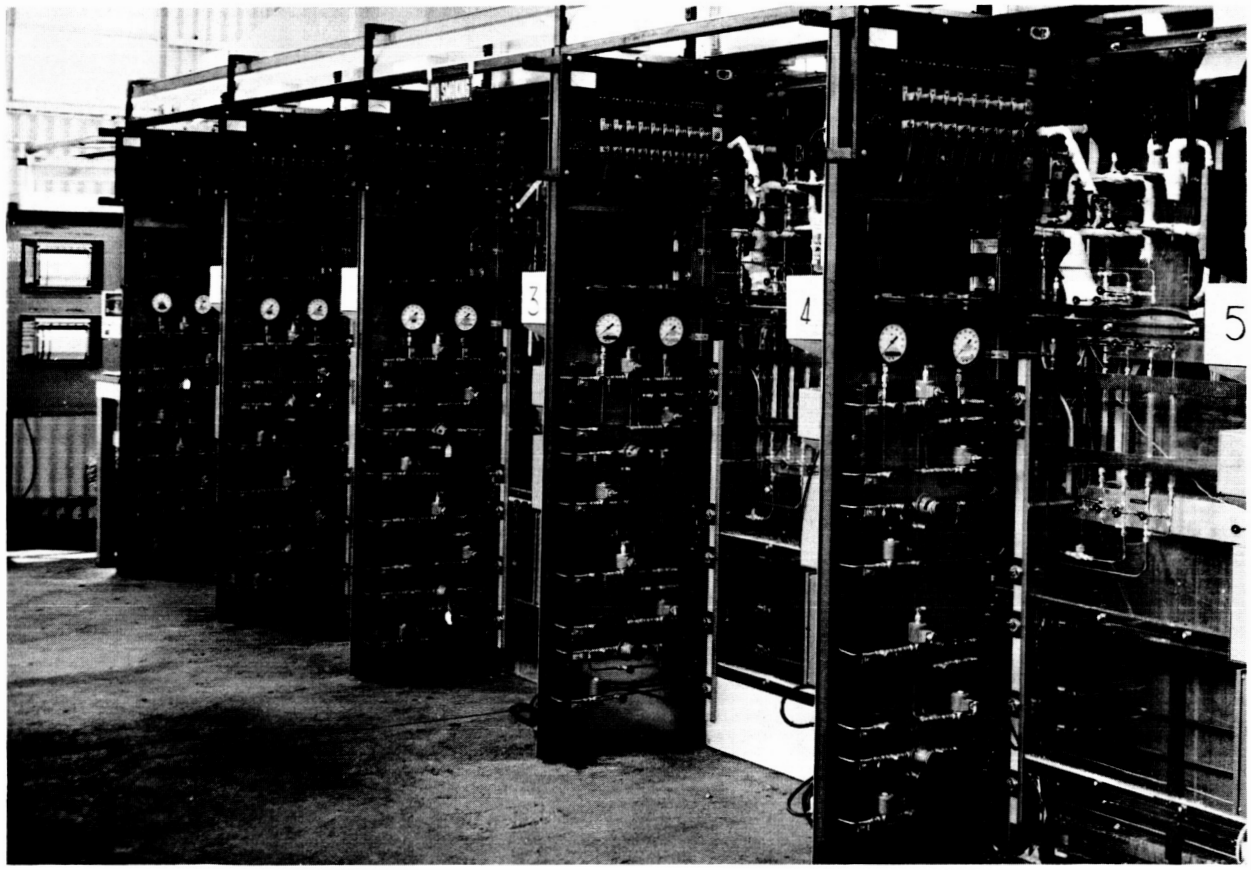


Figure 4-1

LARGE CELL PRESSURE LIFE TEST STATION

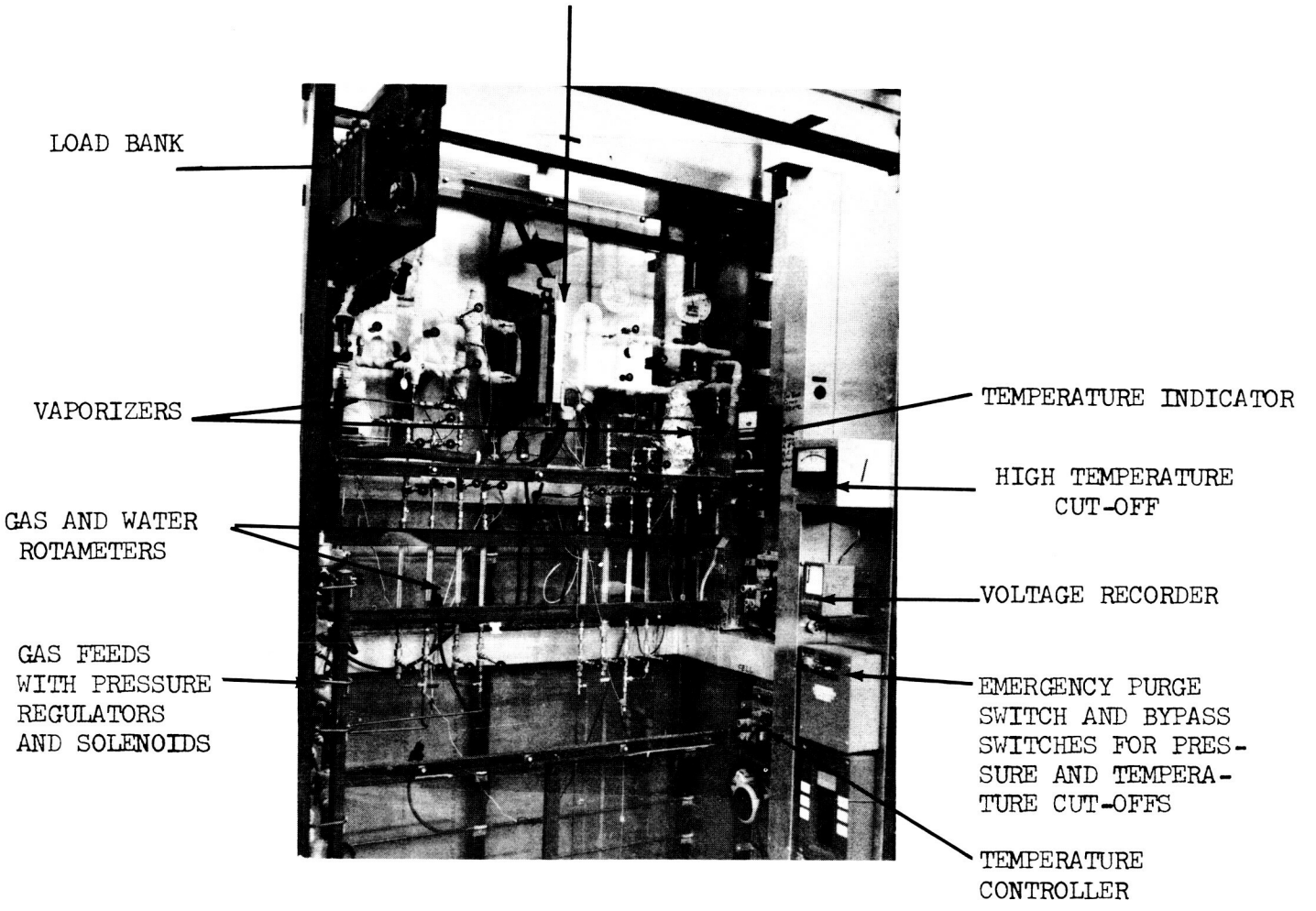


Figure 4-2

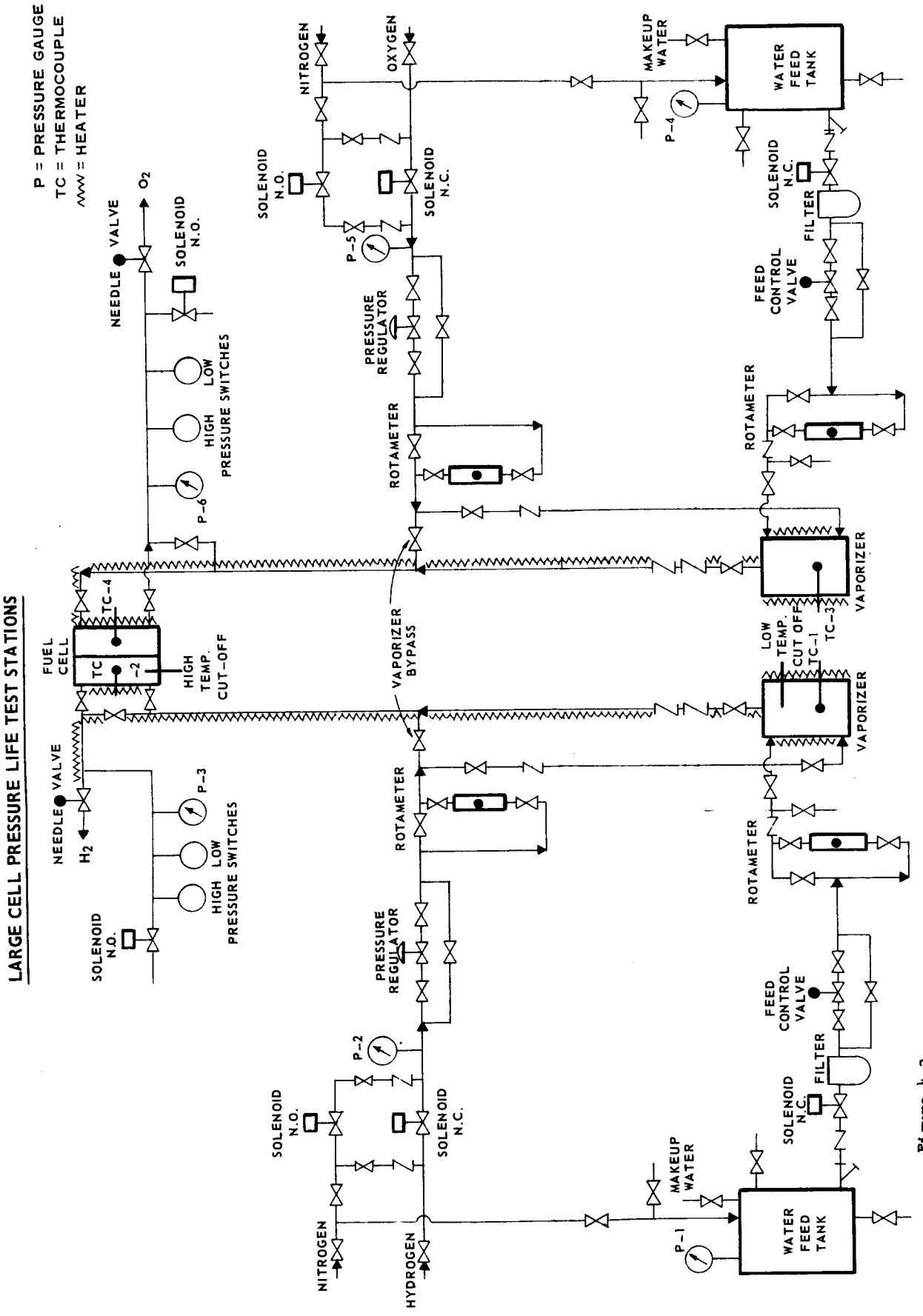

LARGE CELL PRESSURE LIFE TEST STATIONS
P = PRESSURE GAUGE
TC = THERMOCOUPLE
HEATER
NEEDLE VALVE
O_2
SOLENOID N.O.
HIGH LOW PRESSURE SWITCHES
P-6
NITROGEN
OXYGEN
SOLENOID N.O.
SOLENOID N.C.
P-5
PRESSURE REGULATOR
ROTAMETER
MAKEUP WATER
P-4
WATER FEED TANK
SOLENOID N.C.
FILTER
FEED CONTROL VALVE
FUEL CELL
TC-4
TC-2
HIGH TEMP. CUT-OFF
VAPORIZER BYPASS
VAPORIZER
LOW TEMP. CUT OFF
TC-1
TC-3
NEEDLE VALVE
H_2
P-3
HIGH LOW PRESSURE SWITCHES
SOLENOID N.O.
P-2
SOLENOID N.C.
NITROGEN
HYDROGEN
MAKEUP WATER
P-1
WATER FEED TANK
SOLENOID N.C.
FILTER
FEED CONTROL VALVE

Figure 4-3

VAPORIZER DESIGN

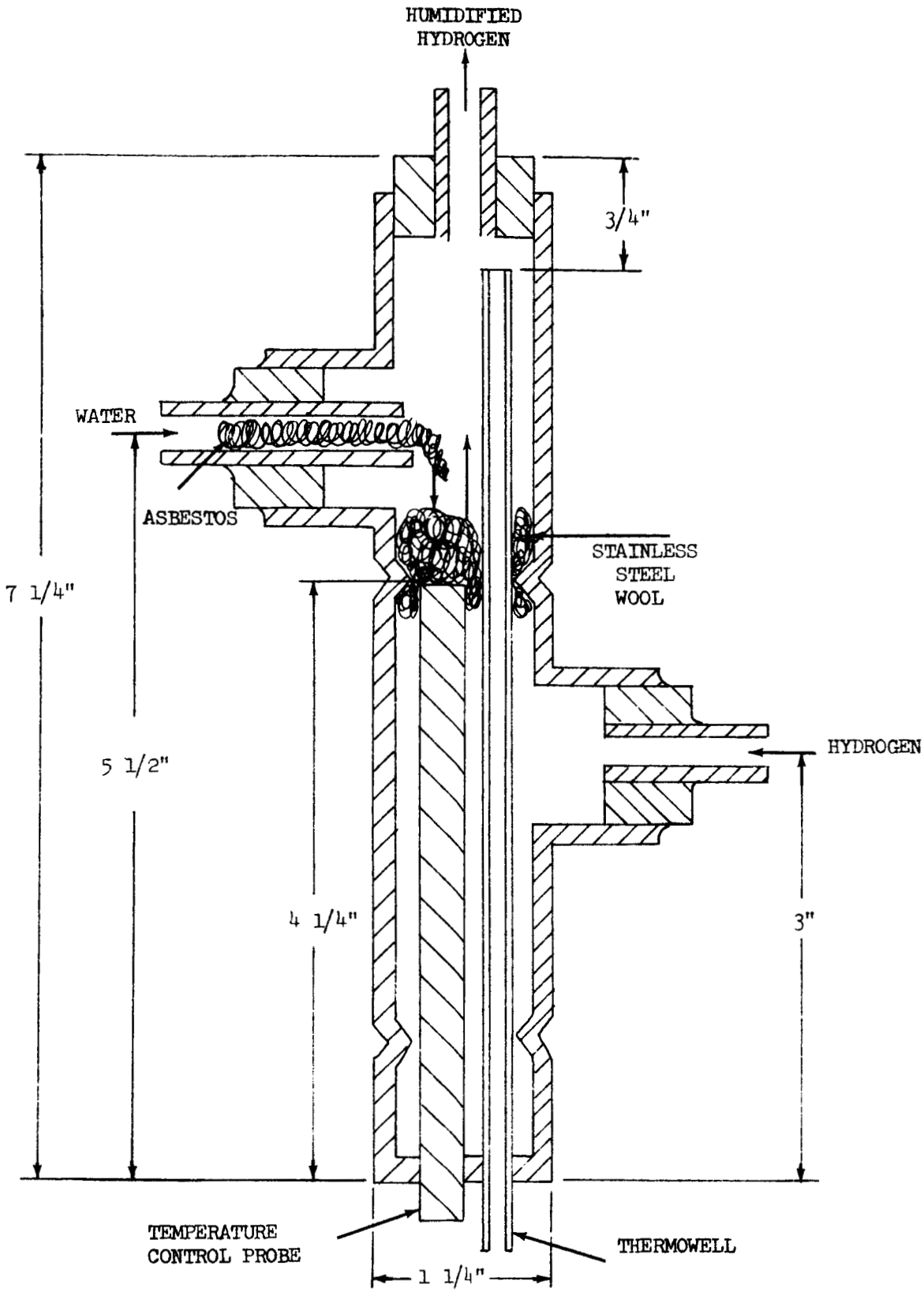


Figure 4-4

SIX INCH PRESSURE CELL: ORIGINAL

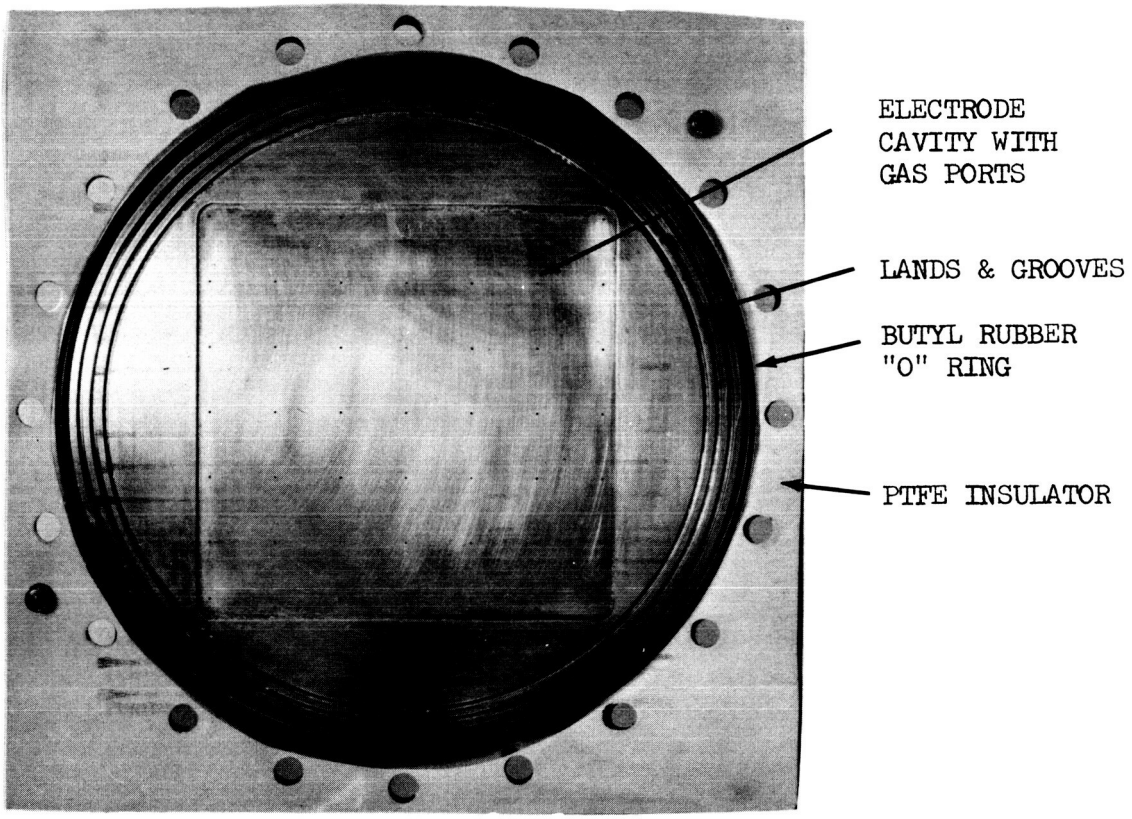


Figure 4-5

SIX INCH PRESSURE CELL: MODIFIED

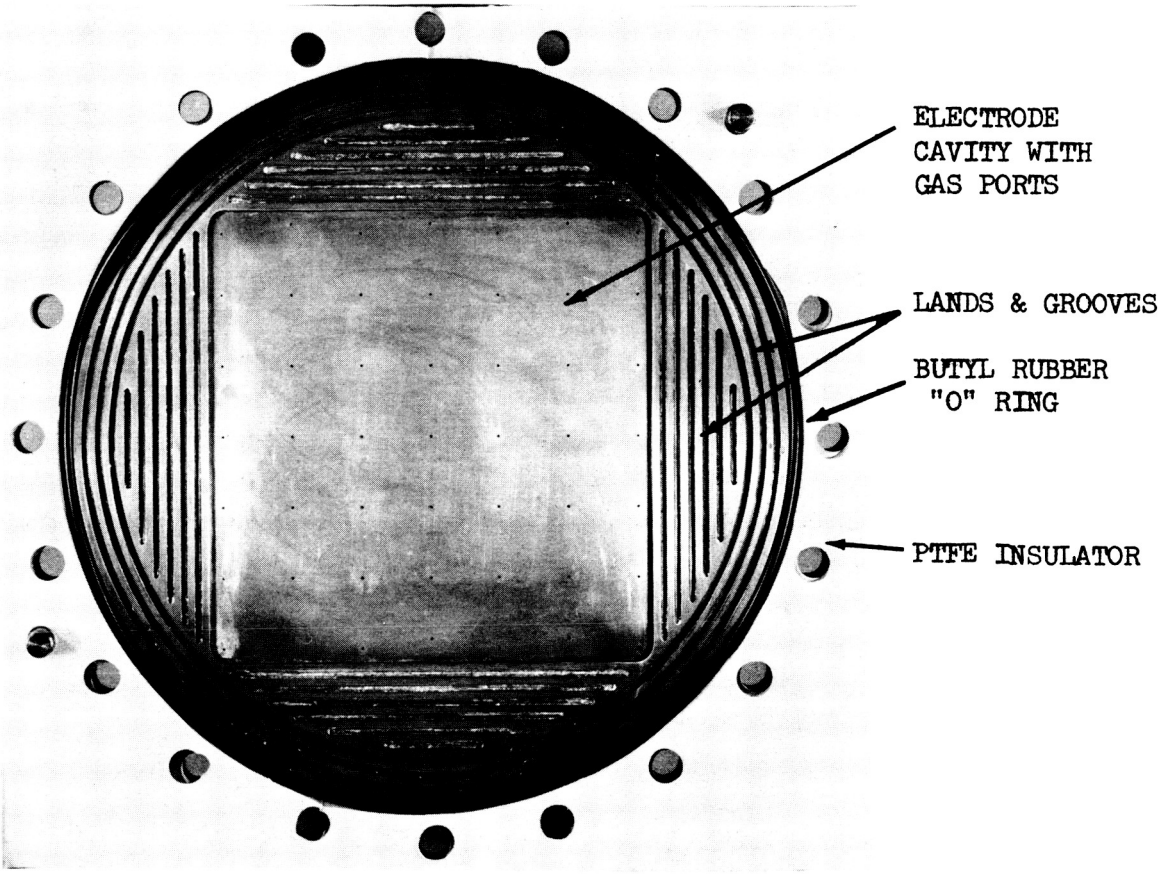
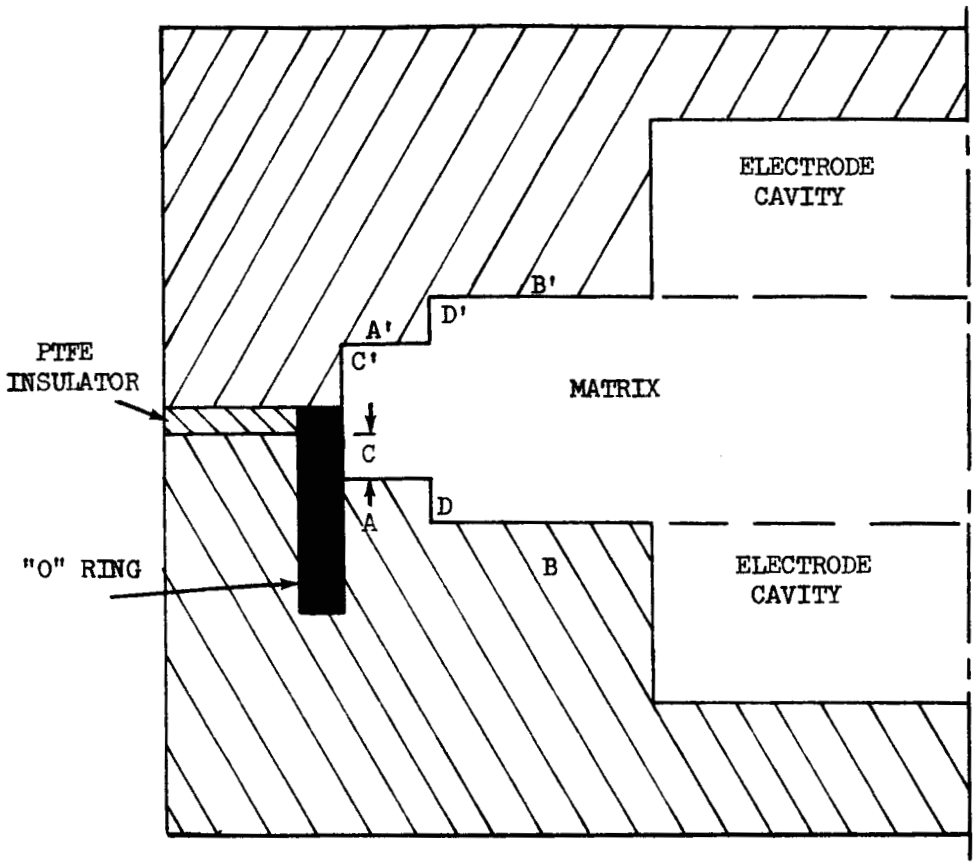


Figure 4-6

LARGE PRESSURE CELLS - CONFIGURATIONS USED FOR TEST ASSEMBLIES



CELL CONFIGURATION NO.	GROOVES IN SECTIONS:	UNDERCUT DIMENSION (MILS) C	D	C'	D'
(1)	A,B,A',B'	5	5	8	4
(2)	A,B,A'	6	2	8	4
(3)	A,B	0	5	0	5
(4)	A,A'	0	5	0	5
(5)	A,A'	6	2	5	5

(a) Sections A and A' are circular.

(b) Sections B and B' are segmental.

Figure 4-7

INITIAL PERFORMANCE OF QUINTERRA ASBESTOS MATRIX

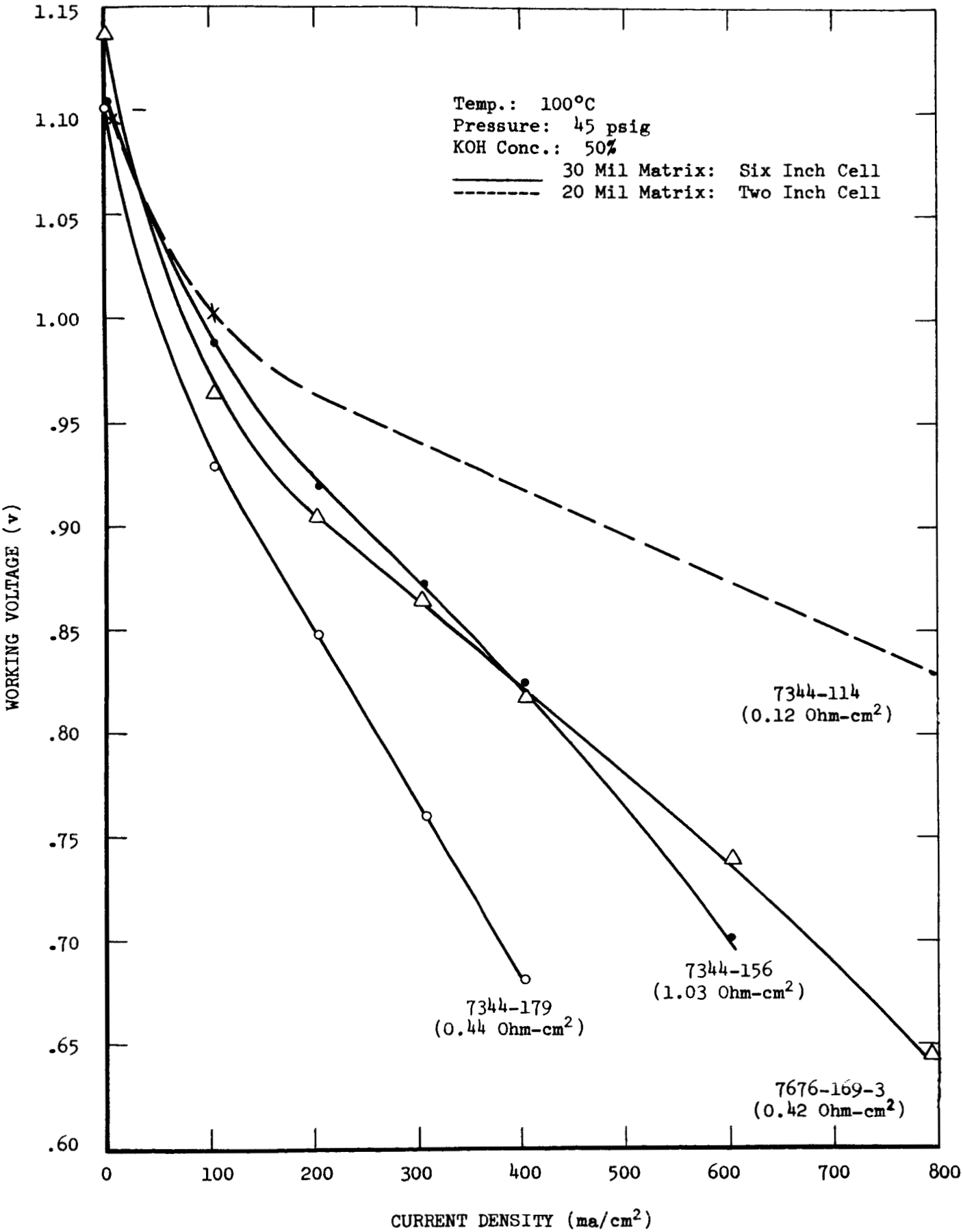


Figure 4-8

INITIAL POLARIZATION OF FUEL CELL ASBESTOS MATRIX

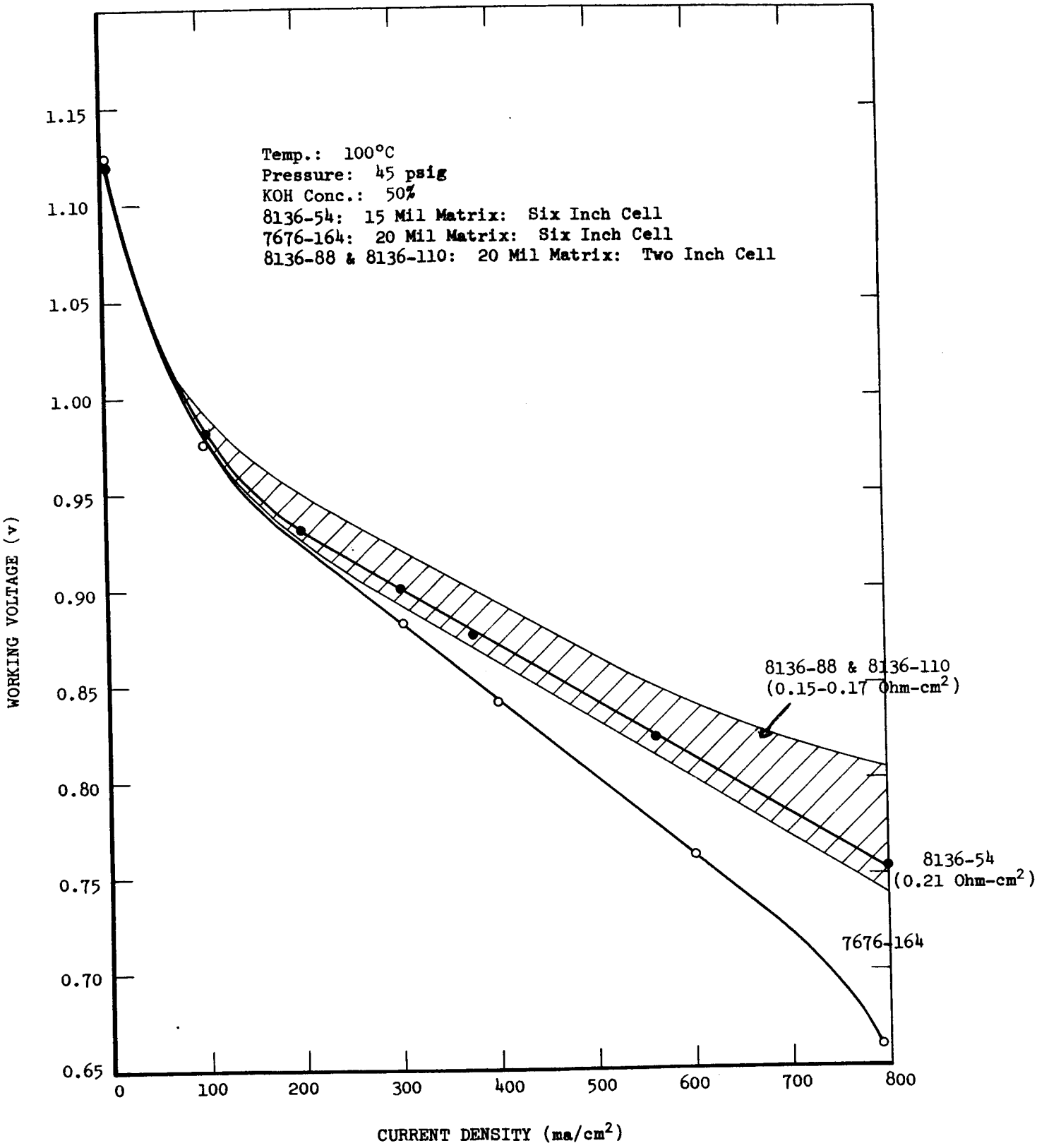


Figure 4-9

LARGE CELL PRESSURE LIFE TESTS

Pressure: 45 psig
8136-54: 15 Mil Fuel Cell Asbestos Matrix: 100°C: 50% KOH
8136-96: 20 Mil Ceria-PTFE Matrix: 125°C: 50% KOH

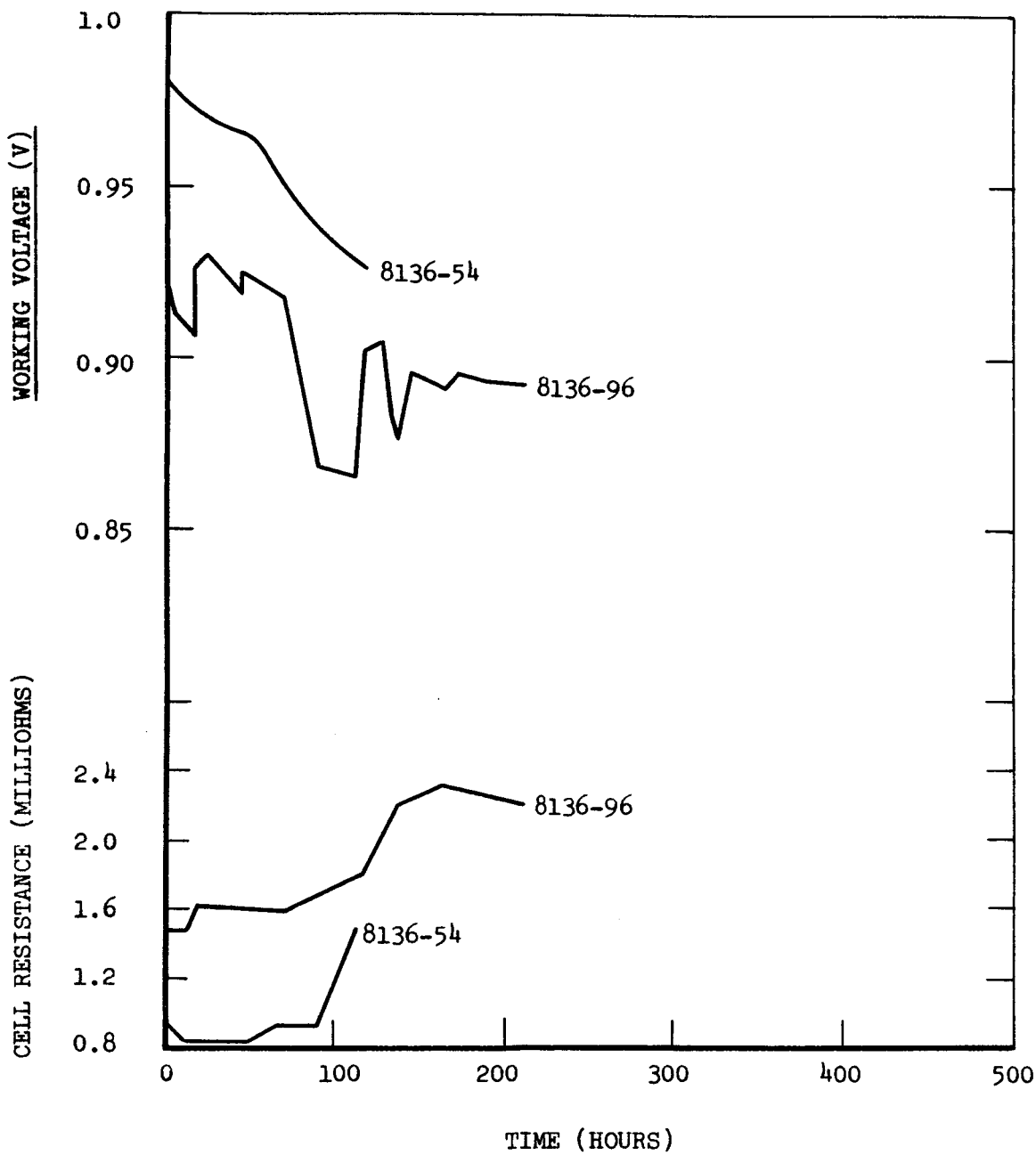


Figure 4-10

5. REFERENCES

1. "Research and Development of High-Performance Light-Weight Fuel Cell Electrodes," American Cyanamid Company, Final Report, November 1, 1963 to October 31, 1964, NASA-CR 54436.

2. "Development of High-Performance Light-Weight Electrodes for Hydrogen-Oxygen Fuel Cells," American Cyanamid Company, Final Report, April 1, 1965 to June 31, 1966, NASA-CR 72166.

3. International Critical Tables, 3, 373, (1928).

4. J. E. Clifford and C. L. Faust, Research on the Electrolysis of Water with a Hydrogen Diffusion Cathode to be used in a Rotating Cell, Battelle Memorial Inst., Final Report, June 1, 1961 to May 31, 1962, (Contract AF 33 (616) 8431, Project 6373 (AMRI-TDR 62-94).